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glacial acetic acid, but dissolved more readily in chloroform; it dissolved in concentrated sulphuric acid to a reddish-purple solution.

6-Chloro-m-4-xylyl n-Propyl Ketone (XXI).—The replacement of the amino-group by chlorine was effected by the Sandmeyer reaction. This chloro-derivative was obtained by distillation in steam as an almost colourless oil, solidifying on cooling to 0° . Two crystallisations from alcohol at temperatures below 0° furnished a white, crystalline powder melting at $9-10^{\circ}$ (Found: Cl = 16.44. $C_{12}H_{13}OCl$ requires Cl = 16.83 per cent.). This substance had a characteristic odour similar to that of honey, but not so powerful as that of 4-chlorophenyl *n*-propyl ketone.

Oxidation with chromic acid solution gave an acid which crystallised from alcohol in small, white needles melting at 165° after one crystallisation. This acid is presumably *5-chloro-2:4-dimethylbenzoic acid*, which does not appear to have been previously described.

2:6-Dinitro-m-4-xylyl n-Propyl Ketone (XX).—*m*-4-Xylyl *n*-propyl ketone (1 gram) was nitrated by adding its solution in 9 grams of concentrated sulphuric acid to a mixture of 10.5 grams of nitric acid (*d* 1.5; free from nitrous acid) and 27 grams of sulphuric acid, cooled to -12° , and stirred continuously. On pouring on to ice, a milky, semi-solid mass separated, which was taken up with ether and washed successively with sodium carbonate solution, dilute sodium hydroxide, and water. Evaporation of the solvent gave *2:6-dinitro-m-4-xylyl n-propyl ketone* as a pale yellow oil which solidified after two or three weeks; it separated from alcohol in a mass of white, hair-like needles melting at 63° (Found: N = 10.78. $C_{12}H_{14}O_5N_2$ requires N = 10.52 per cent.).

IV. *p*-Dibutylbenzene (XXII).

p-Di-*n*-butylbenzene was prepared by the action of sodium on a mixture of *p*-dichlorobenzene and *n*-butyl chloride. The yield, however, was small, and the numerous by-products obtained added to the difficulty of isolating the hydrocarbon in a pure state.

The reaction was carried out in a capacious flask immersed in an oil-bath, heated to 110° and subsequently to 150° . *n*-Butyl chloride (2 grams) and *p*-dichlorobenzene (60 grams) dissolved in 50 c.c. of xylene were gradually added to 50 grams of sodium shavings covered with xylene (75 c.c.), so that the heat of the reaction was just sufficient to keep the solvent boiling. The product was filtered to remove sodium and sodium chloride, and the cake of mineral matter was extracted thoroughly with warm benzene. After the bulk of the solvent had been removed from the combined extract

and washings, a dark brown, viscous residue remained, having a faintly green appearance in reflected light. The product was distilled, fractions being collected up to 280–300°. By means of a lengthy process of fractionation, followed by treatment with metallic sodium, *p-di-n-butylbenzene* was obtained boiling at 224–225.5°/759 mm. (Found: C = 88.75, 88.76; H = 10.95, 11.30. $C_{14}H_{22}$ requires C = 88.34; H = 11.66 per cent.). After further distillations, the hydrocarbon gave C = 88.65; H = 11.3 per cent. Appreciable quantities of diphenyl were obtained in the reaction, and no doubt the presence of traces of diphenyl accounts for the high carbon content of the hydrocarbon. *p-Di-n-butylbenzene* is a colourless liquid having a faint, agreeable, orange-like odour.

2-Nitro-1:4-di-n-butylbenzene.—Dibutylbenzene (7 grams) was cooled to 0° and fuming nitric acid added in small quantities until 20 grams had been used. At the commencement of the operation the acid layer became dark red. The hydrocarbon on the other hand darkened as the nitration proceeded, until it was almost indistinguishable from the lower stratum. The nitration was checked as soon as nitrous fumes were evolved and the upper layer became lighter in colour. The crude nitro-compound was separated and treated repeatedly with water and sodium hydroxide solution until the washings were not tinted red. It was purified by distillation in steam, when *2-nitro-1:4-di-n-butylbenzene* was obtained as a pale yellow, refractive liquid, having a pleasant and characteristic odour, faintly resembling that of lemons. It was purified for analysis by further distillation in steam, the first and the last portions of the distillate being rejected (Found: N = 6.14. $C_{14}H_{21}O_2N$ requires N = 5.95 per cent.).

2-Amino-1:4-di-n-butylbenzene (XXIII).—The reduction of *2-nitro-1:4-dibutylbenzene* to the corresponding amino-compound did not proceed smoothly when zinc dust and ammonium chloride, or tin or zinc with aqueous or alcoholic hydrochloric acid were employed as reducing agents. More favourable results were obtained by the use of iron filings and acetic acid, but even under these conditions the product was contaminated with appreciable quantities of a less basic substance.

The nitro-compound (6.4 grams), dissolved in 15 c.c. of glacial acetic acid, was gradually added to 15 grams of iron filings covered with 50 grams of 80 per cent. acetic acid. The mixture was gently heated during the addition of the nitrodibutylbenzene and for a period of one hour after all the nitro-compound had been added. The bulk of the acetic acid was removed by distillation, and the crude amine isolated by distillation in steam after making the residue

alkaline. It was partly purified by conversion into the sparingly soluble *sulphate*, which was extracted with ether. From the sulphate a moderately pure specimen of the base was obtained as a colourless liquid having a faint yet characteristic odour somewhat resembling that of mushrooms. The *hydrochloride*, which is soluble in water or chloroform, separated from dilute hydrochloric acid in white, flattened needles.

2-Benzoylamino-1:4-di-n-butylbenzene, after repeated crystallisation from alcohol, separated in white masses of needles melting at 116° (Found: C = 81.4; H = 8.6. $C_{21}H_{27}ON$ requires C = 81.5; H = 8.8 per cent.).

We desire to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant which has partly defrayed the expense of this investigation.

THE CHEMICAL DEPARTMENT,
THE UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

(Received, October 19th, 1921.)

CCXVII.—The Nitro- and Amino-derivatives of 4-Phenyglyoxaline.

By REGINALD LINDSAY GRANT and FRANK LEE PYMAN.

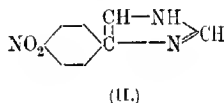
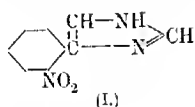
THE laws of substitution in the glyoxaline nucleus, and the properties conferred by it upon substituents in the 2- and 4- (or 5-), positions have been the subjects of previous papers by one of us, and Dr. R. G. Fargher, and are being further investigated in these laboratories. The present work was carried out with the object of contributing to our present scanty knowledge of the somewhat unstable 4-aminoglyoxalines. The simplest member of the series is unknown, and the only substance which is known certainly to belong to this class is 4-amino-5-methylglyoxaline (Fargher, T., 1920, **117**, 668), although the same author (*loc. cit.*) has shown that the reduction product of 4-*p*-bromobenzeneazo-2-phenylglyoxaline (Fargher and Pyman, T., 1919, **115**, 258) is probably 5-amino-4-(5'-bromo-2'-aminophenyl)-2-phenylglyoxaline.

It was thought that a 4-amino-derivative of a 5-phenyl (or substituted phenyl)-glyoxaline might be stable and consequently 4-phenylglyoxaline was chosen as the starting material. This substance has been prepared previously by Pinner (*Ber.*, 1902, **35**,

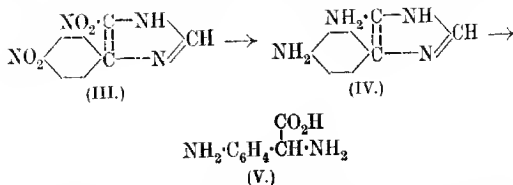
4131) by the action of ammonia on phenylglyoxal, but is more conveniently prepared by the application of Gabriel's method (*Ber.*, 1894, 27, 1037) for the synthesis of glyoxalines, a method which has been employed for the synthesis of derivatives of 4-phenylglyoxaline, substituted in the benzene nucleus, by Stephen and Weizmann (*T.*, 1914, 105, 1046).

The interaction of ω -aminoacetophenone hydrochloride and potassium thiocyanate leads through ω -aminoacetophenone thiocyanate to 2-thiol-4-phenylglyoxaline, which readily gives 4-phenylglyoxaline on oxidation.

Nitration of this substance, conveniently effected by dissolving its nitrate in sulphuric acid and heating the solution, yields a mixture of two mononitro-derivatives, which give on oxidation *o*- and *p*-nitrobenzoic acids respectively and are therefore 4-*o*- and 4-*p*-nitrophenylglyoxalines (I and II).

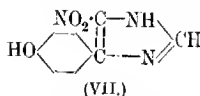
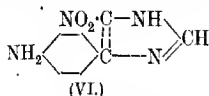


Further nitration of 4-*p*-nitrophenylglyoxaline by the same method effects the introduction of a nitro-group into the glyoxaline nucleus, for the dinitrophenylglyoxaline obtained in this way yields *p*-nitrobenzoic acid almost quantitatively on oxidation. The fact that glyoxalines can be nitrated in the 4- (or 5-) but not in the 2-position indicates that this substance is 5-nitro-4-*p*-nitrophenylglyoxaline (III) and confirmation of this view was obtained by the complete reduction of the substance, when a diamino-4-phenylglyoxaline resulted which was not identical with 2-amino-4-*p*-aminophenylglyoxaline (Fargher and Pyman, *loc. cit.*), and was consequently 5-amino-4-*p*-aminophenylglyoxaline (IV). The dihydrochloride of this base is stable in aqueous solution, but undergoes decomposition when heated with hydrochloric acid at 170°, yielding ammonia and *p*-aminophenylaminoacetic acid (V).



A further study of the preparation and properties of the diamine is contemplated.

Partial reduction of 5-nitro-4-*p*-nitrophenylglyoxaline by means of alcoholic ammonium sulphide led to the isolation of 5-nitro-4-*p*-aminophenylglyoxaline (VI), the constitution of which follows from the facts (1) that its *acetyl* derivative gave a small quantity of *p*-acetylaminobenzoic acid on oxidation; (2) that it was unaffected by concentrated hydrochloric acid at 170°, unlike the diamine. Replacement of the amino-group of this substance by the hydroxy-group gave 5-nitro-4-*p*-hydroxyphenylglyoxaline (VII).



In the course of this work, it was found that 4-phenylglyoxaline and its mononitro-derivatives gave the corresponding *N*-benzoyl derivatives when submitted to benzoylation by the Schotten-Baumann method, whereas in all previous applications of this method of benzoylation to glyoxalines, either derivatives of dibenzoylaminoethylene have been obtained, as in the case of glyoxaline itself (Bamberger and Berlé, *Annalen*, 1892, **273**, 342) and 4-methylglyoxaline (Windaus and Knoop, *Ber.*, 1905, **38**, 1166), or the substance has been recovered unchanged (Windaus, *Ber.*, 1909, **42**, 758; 1910, **43**, 499).

EXPERIMENTAL.

2-Thiol-4-phenylglyoxaline.

Concentrated aqueous solutions containing 30 grams of ω -aminoacetophenone hydrochloride and 17 grams of potassium thiocyanate respectively were mixed, and the liquor (L) evaporated to dryness on a water-bath. The residue was extracted with water, when 24.5 grams of crude 2-thiol-4-phenylglyoxaline remained in the form of small reddish-brown plates, melting at 254°. The yield thus amounts to 79 per cent. of the theoretical. After recrystallisation from alcohol (with the aid of animal charcoal), the substance was obtained in colourless plates, melting at 261° (corr.) (Found: C = 61.5, 61.4; H = 4.8, 4.5; N = 15.8, 15.7. $C_9H_8N_2S$ requires C = 61.3; H = 4.6; N = 15.9 per cent.). It is very sparingly soluble in cold water, readily soluble in acetone or alcohol, less readily so in ether, and very sparingly soluble in chloroform or benzene.

It is soluble in concentrated hydrochloric acid, forming a *hydrochloride*, which crystallises in clear prisms melting at 252° (corr.) and dissociates on the addition of water. It is soluble in dilute

aqueous ammonia or sodium hydroxide, but not in cold aqueous sodium carbonate. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The *picrate* is obtained in garnet-red, hexagonal tablets, melting at 182° (corr.), on mixing molecular proportions of the constituents in concentrated absolute alcoholic solution. When dissolved in hot water, it dissociates into its components.

An intermediate product in the preparation of 2-thiol-4-phenylglyoxaline can be isolated by concentrating the liquor (L) to a small volume under diminished pressure, when on cooling *o*-aminoacetophenone thiocyanate separates in long, colourless needles, melting at 135° (corr.) (Found: C = 55.5, 55.6; H = 5.3, 5.2; N = 14.2, 14.2. $C_9H_{10}ON_2S$ requires C = 55.6; H = 5.2; N = 14.4 per cent.). It is readily soluble in water, and is unstable, being readily converted into 2-thiol-4-phenylglyoxaline by heating at 100°. The possibility that this compound was the isomeric thiocarbamide is eliminated by the fact that it gives a deep red colour with ferric chloride, and can be readily converted into *o*-aminoacetophenone picrate, which melts at 174° (corr.).

4-Phenylglyoxaline.

Twenty-four grams of crude 2-thiol-4-phenylglyoxaline (m. p. 254°) were added slowly to 480 c.c. of gently boiling 10 per cent. nitric acid. After being boiled for another fifteen minutes, the liquor was kept and deposited 25 grams of crude 4-phenylglyoxaline nitrate melting at 170°, that is, 88 per cent. of the theoretical yield.

This *nitrate* separates from water in long, pale yellow, prismatic needles, which melt at 179° (corr.). It is soluble in about 8 parts of boiling water, is feebly acid to litmus, and is anhydrous (Found: N = 20.4, 20.3. $C_9H_8N_2HNO_3$ requires N = 20.3 per cent.). The corresponding base was found to melt at 128° (corr.); Pinner (*loc. cit.*) gives 128—129°.

The *hydrochloride* forms long, colourless needles, which melt at 180° (corr.) and are very readily soluble in water. The *hydrogen oxalate* crystallises from water in broad needles, which melt at 199° (corr.), and are only moderately readily soluble in cold water. The *picrate* forms long, yellow needles, which melt at 216° (corr.), and are soluble in about 140 parts of hot water.

4-Phenylglyoxaline gives a deep cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

Nitration of 4-Phenyglyoxaline. Isolation of 4-o- and 4-p-Nitrophenylglyoxalines.

Twenty grams of 4-phenylglyoxaline nitrate were added to 40 c.c. of sulphuric acid, the temperature of the mixture being kept below 30°. The product was heated under reflux for two hours on a water-bath, then diluted with 400 c.c. of water, heated to about 60°, and neutralised by the addition of, first, sodium hydroxide, then sodium carbonate. From the hot solution, 16.8 grams of crude 4-*p*-nitrophenylglyoxaline, melting at 218°, separated, whilst the filtrate on cooling deposited 1.7 grams of the crude *ortho*-isomeride, melting at 134°, a further small quantity of this being obtained on concentrating the liquor. The various crops were converted into the nitrates and fractionated, the bases being then regenerated from the salts and recrystallised. In the case of the *ortho*-compound, crystallisation of the hydrochloride also was effective. By these means, there were isolated in a pure state 12.7 grams of 4-*p*-nitrophenylglyoxaline and 4.6 grams of 4-*o*-nitrophenylglyoxaline, the yields amounting to 60 and 25 per cent. of the theoretical respectively.

4-*o*-Nitrophenylglyoxaline crystallises from alcohol in pale yellow, elongated, glistening plates, which melt at 146° (corr.). In the dry state this base (but not its salts) rapidly turns green under the influence of light, and in strong sunlight becomes dark olive-green in the course of half an hour. It is insoluble in cold, but sparingly soluble in hot, water, very readily soluble in alcohol or acetone, soluble in ether or chloroform, and sparingly soluble in benzene or light petroleum (Found: C = 57.1, 57.0; H = 3.9, 3.7; N = 22.3, 22.3. $C_9H_7O_2N_3$ requires C = 57.1; H = 3.7; N = 22.2 per cent.).

It is readily soluble in dilute mineral acids giving colourless solutions, and in caustic alkalis giving yellow to deep orange solutions. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The hydrochloride crystallises from water in large, clear greenish yellow prisms which melt at 203° (corr.) and are anhydrous. It is very easily soluble in water, giving a strongly acid solution (Found: Cl = 15.5, 15.6. $C_9H_7O_2N_3$, HCl requires Cl = 15.7 per cent.).

The nitrate crystallises from water, in which it is easily soluble, in pale yellow needles, which decompose at about 168° (corr.), and are anhydrous (Found: N = 22.2. $C_9H_7O_2N_3.HNO_3$ requires N = 22.2 per cent.).

4-*p*-Nitrophenylglyoxaline crystallises from alcohol in canary-

yellow needles, which melt at 225° (corr.). It is insoluble in water, even hot, readily soluble in alcohol or acetone, sparingly soluble in ether or chloroform, and only very sparingly so in benzene or light petroleum (Found : C = 56.9, 57.0; H = 3.9, 3.7; N = 22.2, 22.2. $C_9H_7O_2N_3$ requires C = 57.1; H = 3.7; N = 22.2 per cent.).

It is readily soluble in dilute mineral acids giving colourless solutions, and in caustic alkalis giving yellow to deep orange solutions. It gives a cherry-red colour with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The *hydrochloride* forms very pale buff needles from alcohol. It melts at 292° (corr.) and is anhydrous. It is very easily soluble in water giving a strongly acid solution, and easily soluble in hot alcohol (Found : C = 47.7; H = 3.6; N = 18.6, 18.7; Cl = 15.7. $C_9H_7O_2N_3.HCl$ requires C = 47.9; H = 3.6; N = 18.6; Cl = 15.7 per cent.).

The *nitrate* crystallises from water in pale yellow needles, which melt at 200° (corr.). It is soluble in about 25 parts of boiling water and is anhydrous (Found : N = 22.2. $C_9H_7O_2N_3.HNO_3$ requires N = 22.2 per cent.).

Nitration of 4-p-Nitrophenylglyoxaline. Isolation of 5-Nitro-4-p-nitrophenylglyoxaline.

Twenty grams of 4-*p*-nitrophenylglyoxaline nitrate were added to 40 c.c. of sulphuric acid, and the mixture was heated under reflux for two hours on a water-bath. After cooling, the mixture was diluted with 400 c.c. of water, when a cream-coloured precipitate was obtained. This was extracted with hot dilute hydrochloric acid and left 17.2 grams of the nearly pure dinitro-compound, whilst 0.9 gram of pure 4-*p*-nitrophenylglyoxaline was isolated from the mother-liquors. The yield, allowing for the recovered material, is almost quantitative.

5-Nitro-4-*p*-nitrophenylglyoxaline crystallises from alcohol in colourless needles which melt at 293° (corr.). It is insoluble in cold and very sparingly soluble in boiling water, fairly easily soluble in alcohol or acetone, sparingly soluble in ether, and very sparingly so in chloroform (Found : C = 46.0, 46.1; H = 2.6, 2.6; N = 24.0, 24.1. $C_9H_6O_4N_4$ requires C = 46.1; H = 2.6; N = 23.9 per cent.).

It is soluble in strong mineral acids, but is precipitated unchanged on the addition of water; it dissolves in dilute aqueous ammonia, sodium carbonate, or sodium hydroxide, giving yellow solutions. The sodium, potassium, and ammonium salts form pale yellow

needles and are sparingly soluble in cold water. It gives no coloration with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate.

The *nitrate* crystallises from 50 per cent. nitric acid in large, flat needles. It dissociates on treatment with water, or when heated at 100° , the residue consisting of the base (Found: loss at $100^{\circ} = 21.2$. $C_9H_6O_4N_4 \cdot HNO_3$ requires loss of $HNO_3 = 21.2$ per cent.).

Benzoylation of 4-Phenylglyoxaline and its Nitro-derivatives.

When treated with benzoyl chloride and aqueous sodium hydroxide at the laboratory temperature, 4-phenylglyoxaline and its *o*- and *p*-nitro-derivatives gave benzoyl derivatives, which, after washing with a little ether, were obtained in yields of 90–97 per cent. of the theoretical, the crude products melting at 120° , 97° , and 176° respectively. After recrystallisation from alcohol, the products were as follows:

1. *Benzoyl-4* (or 5)-*phenylglyoxaline* (*A*).—Colourless needles melting at 132° (corr.) (Found: C = 77.2, 77.4; H = 4.8, 4.9; N = 11.1, 11.2. $C_{16}H_{12}ON_2$ requires C = 77.4; H = 4.9; N = 11.3 per cent.).

1. *Benzoyl-4* (or 5)-*o*-nitrophenylglyoxaline (*B*).—Elongated plates, which melt at 100 – 101° (corr.) (Found: C = 65.4, 65.4; H = 3.8, 3.7; N = 14.2, 14.2. $C_{16}H_{11}O_3N_3$ requires C = 65.5; H = 3.8; N = 14.3 per cent.).

1. *Benzoyl-4* (or 5)-*p*-nitrophenylglyoxaline (*C*).—Pale yellow, flat needles, melting at 182° (corr.) (Found: C = 65.5, 65.4; H = 3.9, 3.8; N = 14.2, 14.2. $C_{16}H_{11}O_3N_3$ requires C = 65.5; H = 3.8; N = 14.3 per cent.).

The three benzoyl derivatives are insoluble in water or dilute aqueous sodium hydroxide, easily soluble in hot alcohol, and sparingly soluble in ether. They differ in stability. A pure sample of *A*, kept for four weeks in a well-corked bottle, had become almost converted into an oil, from which 4-phenylglyoxaline and benzoic acid were isolated. Moreover, this substance can be recrystallised from alcohol only in small yield owing to hydrolysis. *B* and *C* are stable when pure, and *C* is decomposed to a much smaller extent than *A* on boiling with alcohol, whilst *B* scarcely suffers hydrolysis under these conditions. All three compounds are rapidly hydrolysed by hot dilute hydrochloric acid.

5-Nitro-4-*p*-nitrophenylglyoxaline was recovered unchanged after treatment with benzoyl chloride and aqueous sodium hydroxide.

Oxidation of the Nitro-derivatives of 4-Phenylglyoxaline.

The nitro-derivatives of 4-phenylglyoxaline (1/100 gram-mol.) were dissolved in 250 c.c. of boiling water containing one equivalent of potassium hydroxide, and oxidised with the calculated quantity (4.2 grams) of potassium permanganate. Under these conditions 4-*p*-nitrophenylglyoxaline and 5-nitro-4-*p*-nitrophenylglyoxaline each gave *p*-nitrobenzoic acid in almost quantitative yield; the crude acid (of which the main crops melted at 232° and 226° in the two cases) amounted to 1.65 grams in each case and readily gave the pure acid, which melted at 237° (corr.), alone and when mixed with a reference specimen. 4-*o*-Nitrophenylglyoxaline under the same conditions gave an oily acid which reduced permanganate, and on further treatment with this reagent gave *o*-nitrobenzoic acid, melting at 147° (corr.), alone or mixed with a reference specimen, in a yield of 45 per cent. of the theoretical.

5-Amino-4-p-aminophenylglyoxaline.

Seven grams of 5-nitro-4-*p*-nitrophenylglyoxaline were gradually added to a solution of 42 grams of hydrated stannous chloride in 105 c.c. of hydrochloric acid, the temperature being kept below 15°. The crystalline stannichloride, which separated on heating, was deprived of tin, when 2.8 grams of 5-amino-4-*p*-aminophenylglyoxaline dihydrochloride were obtained, that is, 37 per cent. of the theoretical yield.

5-Amino-4-*p*-aminophenylglyoxaline dihydrochloride crystallises from water in colourless, prismatic needles, which darken at about 260°, but do not melt at 300°. This salt is anhydrous, very easily soluble in water, and very sparingly so in absolute alcohol (Found: C = 43.6, 43.6; H = 5.1, 5.0; N = 22.5, 22.5; Cl = 28.8, 29.4. $C_8H_{10}N_4 \cdot 2HCl$ requires C = 43.7; H = 4.9; N = 22.7; Cl = 28.7 per cent.). Aqueous solutions of the salt give (1) with alkalis, no precipitate, but slowly become oxidised in the air, turning pink and then purple; (2) with nitrous acid, a yellow solution which gives with aqueous sodium hydroxide a clear purple-red solution, and with aqueous sodium β -naphthoxide a sparingly soluble, purple precipitate; (3) with sodium diazobenzene-*p*-sulphonate in the presence of sodium carbonate, a deep reddish-brown solution; (4) with sodium nitroprusside, no colour, but on subsequent addition of sodium hydroxide, an intense dull-brown solution; (5) with sodium acetate and benzaldehyde, a yellow, crystalline benzylidene derivative; (6) with picric acid, a picrate, which crystallises from

water in greenish-yellow needles and does not melt at 300° ; (7) with sulphuric acid, a very sparingly soluble sulphate forming colourless, glistening needles.

Action of Hydrochloric Acid at 170° .—One gram of the diamine dihydrochloride and 10 c.c. of concentrated hydrochloric acid were heated for three hours at 170° . The product consisted of 0.7 gram of colourless crystals and a mother-liquor which gave a residue of 0.6 gram, largely ammonium chloride. The mode of formation and the properties of the former substance indicate that it is *p-aminophenylaminoacetic acid dihydrochloride*. It was recrystallised from dilute hydrochloric acid and formed colourless, prismatic needles which did not melt at 250° , and were anhydrous (Found: Cl = 29.9. $C_8H_{10}O_2N_2 \cdot 2HCl$ requires Cl = 29.7 per cent.). It was easily soluble in water and strongly acid. After diazotisation, it coupled with β -naphthol. When mixed with sodium acetate in concentrated aqueous solution until no longer acid to methyl-orange, the sparingly soluble *monohydrochloride* separated in colourless, glistening plates which had no sharp melting point, but began to turn brown at about 200° and were completely decomposed at 250° (Found: C = 47.4; H = 5.4; N = 13.8. $C_8H_{10}O_2N_2 \cdot HCl$ requires C = 47.2; H = 5.5; N = 13.7 per cent.).

5-Nitro-4-p-aminophenylglyoxaline.

Five grams of 5-nitro-4-p-nitrophenylglyoxaline were dissolved in 700 c.c. of alcohol and 25 c.c. of aqueous ammonia (d 0.880), and hydrogen sulphide was passed through the solution for two hours. The solution was then boiled under reflux for half an hour and kept. The red precipitate was collected, and extracted with 10 per cent. aqueous hydrochloric acid, which removed 3.2 grams of nitro-aminophenylglyoxaline dihydrochloride, that is, 53 per cent. of the theoretical yield.

5-Nitro-4-p-aminophenylglyoxaline dihydrochloride crystallises from dilute hydrochloric acid in yellow, prismatic needles, which turn red at about 220° and decompose at about 256° (corr.) (Found: C = 38.9, 38.9; H = 3.8, 3.6; N = 20.2, 20.2; Cl = 25.3, 25.4. $C_8H_8O_2N_4 \cdot 2HCl$ requires C = 39.0; H = 3.6; N = 20.2; Cl = 25.6 per cent.). It is easily soluble in dilute hydrochloric acid, but dissociates on the addition of water, yielding the base as a bright terracotta precipitate, almost insoluble in water or the usual organic solvents, even when hot (Found: in base dried at 100° , C = 52.8, 52.6; H = 3.9, 3.8; N = 27.3, 27.3. $C_9H_8O_2N_4$ requires C = 52.9; H = 4.0; N = 27.5 per cent.). This is soluble in sodium hydroxide or ammonia (but not in sodium carbonate), giving yellow to

red solutions; the sodium salt crystallises from water in red needles.

Solutions of the hydrochloride in dilute hydrochloric acid give (1) no change in colour on the addition of sodium nitrite, but on adding this solution to aqueous sodium hydroxide, a deeper yellow colour, and on adding it to aqueous sodium β -naphthoxide, a reddish-brown solution, (2) on the addition of aqueous sodium hydroxide, a reddish-brown colour with sodium diazobenzene-*p*-sulphonate in aqueous sodium carbonate.

The dihydrochloride is recovered unchanged after heating with 10 parts of concentrated hydrochloric acid for two and a half hours at 170° .

5-Nitro-p-acetylaminophenylglyoxaline, prepared by heating the above dihydrochloride with acetic anhydride and sodium acetate, forms a bright yellow powder, which does not melt at 280° , and is almost insoluble in water and the usual organic solvents, even when hot. It dissolves in concentrated hydrochloric acid, but is reprecipitated on diluting the solution. It is soluble in aqueous ammonia, sodium carbonate, or hydroxide (Found: in substance dried at 100° , C = 53.5, 53.6; H = 4.4, 4.2; N = 22.7, 22.6. $C_{11}H_{10}O_5N_4$ requires C = 53.6; H = 4.1; N = 22.8 per cent.).

Oxidation.—2.46 Grams of the acetyl derivative were dissolved in a solution of 0.56 gram of potassium hydroxide in 100 c.c. of water mixed with a solution of 4.2 grams of potassium permanganate in 105 c.c. of water, and heated for three-quarters of an hour on the water-bath. The manganese hydroxide having been removed, the liquor was acidified with hydrochloric acid, filtered from 0.3 gram of apparently unchanged acetyl derivative, and extracted with ether. The ethereal extract was evaporated and gave 0.1 gram of crude *p*-acetylaminobenzoic acid, melting at 240° . After purification, a small amount of the pure acid was obtained melting at 260° (corr.), alone or when mixed with a specimen of the pure acid from another source. The identification was confirmed by hydrolysis to *p*-aminobenzoic acid, which melted at 190° (corr.), alone or mixed with a specimen of the pure acid from another source.

5-Nitro-4-p-hydroxyphenylglyoxaline separates as a sandy powder in good yield when 5-nitro-4-*p*-aminophenylglyoxaline dissolved in excess of 20 per cent. aqueous sulphuric acid is treated with the equivalent quantity of sodium nitrite, at the ordinary temperature, and the solution is heated and kept. It crystallises from about 1000 parts of boiling water in golden, feathery needles which do not melt at 300° . It is soluble in moderately concentrated acids when hot, and yields a crystalline hydrochloride with concentrated hydrochloric acid. It is soluble in alkalis, even in sodium carbon-

ate, with a deep red colour (Found: N = 19.9. $C_2H_2O_2N_3$ requires N = 20.5 per cent.).

We are indebted to Miss Esther Levin, M.Sc. Tech., for several analyses carried out in connexion with this investigation.

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CCXVIII.—*The Explosion of Acetylene and Nitrogen.* *Part I.*

By WILLIAM EDWARD GARNER and KICHIMATSU MATSUNO.

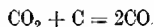
THE observations of Berthelot form the basis of almost every investigation into the phenomena of explosive processes, and it is thus not surprising that the reaction between acetylene and nitrogen was first studied by this great chemist. Berthelot showed that endothermic substances like acetylene, cyanogen, arsenic trihydride, and nitric oxide were readily detonated at atmospheric pressure by means of a fulminate detonator. The detonation could not, however, be brought about by an electric spark, in the case of acetylene, unless the pressure exceeded two atmospheres. A partial decomposition of the acetylene into carbon and hydrogen occurred during sparking, but the heat of decomposition was not liberated sufficiently quickly to start the explosion wave.

When acetylene and nitrogen are sparked at atmospheric pressure, carbon and hydrocyanic acid are produced (Berthelot, *Compt. rend.*, 1868, **67**, 1141). The decomposition of carbon can, however, be avoided and the conversion of acetylene into hydrocyanic acid made quantitative, in the presence of an excess of hydrogen, if the acid is removed by alkali as soon as it is formed. A further study of this reaction was made by Mixer (*Amer. J. Sci.*, 1900, [iv], **9**, 1; 1900, [iv], **10**, 299), who exploded mixtures of acetylene and nitrogen in glass manometers and steel vessels. Both hydrocyanic acid and ammonia were found in the products of explosion. The primary reaction is probably the decomposition of acetylene into hydrogen and carbon, and this is followed by a reaction between the products and nitrogen. At the moment of explosion, among other substances, a mixture of carbon, hydrogen, and nitrogen is obtained, which reacts to give hydrocyanic acid and ammonia. The results of Wallis (*Annalen*, 1906, **345**, 356) and Wartenberg (*Zeitsch. anorg.*

Chem., 1907, 52, 299) on the equilibrium between carbon, hydrogen, and nitrogen will thus be of interest. In these experiments with an equimolecular mixture of hydrogen and nitrogen it was found that about 40 per cent. of hydrocyanic acid was produced at 3300° and 4 per cent. at 1830°.

In many modern explosives, the deficiency of oxygen is so large that carbon is one of the products of detonation. During the cooling of the gases by radiation and by the work done on the container, this carbon reacts with the nitrogen present in the explosive to give hydrocyanic acid. The percentage of this gas in the gaseous products may be quite large, as was shown by Berthelot and Veille in the case of the detonation of benzenediazonium nitrate; 3.2 per cent. of the total gases was hydrocyanic acid. Trinitrotoluene also gives large quantities of hydrocyanic acid on detonation.

The products of an explosive decomposition are very largely determined by the rate of cooling; the slower the rate of cooling of the gases the lower the temperature at which the "chilling" of the gaseous equilibria takes place. This is of special importance in the hydrocyanic acid equilibria in the gases from explosives, for during the cooling a portion of the carbon liberated at the higher temperatures disappears according to the reaction :



The presence of oxygen in the gases introduces a complication into the nitrogen equilibria, which makes their investigation difficult.

It was with the view of throwing light on these complex equilibria, occurring during cooling, that this investigation was undertaken. It was considered that the explosion of acetylene with nitrogen or of cyanogen with hydrogen would give rise to conditions which, while being similar to those occurring in the explosion of high explosives, would be free from the complications due to the presence of oxygen. The effect of the addition of oxygen to the mixture could then be studied.

EXPERIMENTAL.

(a) *Materials*.—The acetylene was obtained from a solution of this gas in acetone kindly supplied by Allen Liversidge, Ltd. Except for the presence of acetone, the gas was almost free from impurities; the first fraction gave 1—2 per cent. of hydrogen and nitrogen, but these constituents rapidly diminished to a negligible quantity as the acetylene was consumed. The percentage of acetylene in the gas liberated is calculated to be approximately 0.5 per cent. at a pressure in the cylinder of 20 atmospheres. It is

thus possible that the gas contained 0.25 per cent. of oxygen, and since the larger portion of this will be burnt to carbon monoxide, the amount of water produced on explosion will be very small. This small quantity of water formed on explosion, however, makes the analysis more difficult, for a mixture of hydrocyanic acid and ammonia in the presence of moisture attacks mercury.

The nitrogen was prepared from ammonium sulphate and sodium nitrite in aqueous solution in the presence of potassium dichromate (Veley, T., 1903, 83, 736); in addition, a little litharge was added. The nitrogen was stored over a suspension of ferrous hydroxide in water to remove nitric acid and to prevent the entrance of oxygen from the air, and was finally dried over phosphoric oxide. The mixtures of nitrogen and acetylene were analysed in a constant-volume apparatus.

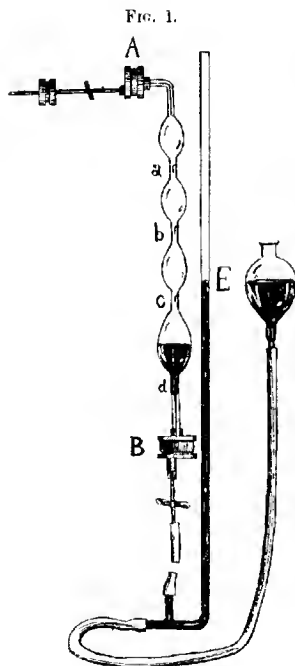
(b) *Bomb*.—Preliminary experiments showed that dry hydrocyanic acid and ammonia were without action on the metals employed in the construction of pressure vessels, and there appeared to be no objection to the use of phosphor-bronze as a bomb material. A phosphor-bronze bomb, similar in design to that used by Wheeler (T., 1918, 113, 855), but with $\frac{3}{8}$ inch in thickness of walls and without the manometer, was obtained from Chas. Cook, the Manchester University Engineering Works. This was 3.988 litres in capacity and held a vacuum for twenty-four hours without appreciable leakage. A little vaselin was all that was necessary to make the joint gas-tight. It was found, however, that a loss of gas occurred at the large joint (annealed copper washer) at the moment of explosion, but as the joint held a vacuum after the experiment, this leakage was not a serious disadvantage.

(c) *Measurement of Pressures*.—Before the gas was introduced, the bomb was evacuated to a pressure of 1 mm. by means of a Cenco-Nelson oil-pump, and the pressure read off on a small McLeod gauge. The dry nitrogen was then introduced, and since the pressure did not reach 1 atmosphere, the measurement of this offered no difficulty. The acetylene was introduced directly into the bomb up to a pressure of 3.4 atmospheres, and after allowing time for the mixing of the gases, a sample was taken for analysis and the pressure measured accurately. For this purpose a new type of manometer was constructed, capable of reading up to five atmospheres. The principle adopted was to expand a known volume of the gas, at the pressure in the bomb, to approximately atmospheric pressure and to measure the new pressure on a mercury-glass manometer. A diagram of the manometer is given in Fig. 1. The apparatus consists of a series of glass bulbs *A* to *B* closed at both ends by two glass-to-metal taps *A* and *B* (*J. Soc. Chem. Ind.*,

1920, 39, 247 π) and attached to the manometer *E*. The volumes enclosed by mercury between the blue-glass tips *a*, *b*, *c*, and *d* and the tap *A*, were accurately determined.

Before the experiment, the apparatus is filled with mercury up to the tip *a*, and the tap *B* is closed. The gases from the bomb are then admitted into the first bulb, and the tap *A* is closed. Since in these experiments the pressure of the gas was 3–3.5 atmo-

spheres, it was allowed to expand to the blue pointer, *c*, by opening the tap *B* and adjusting the level in *E*. The pressure was calculated from this level and the ratio of the volume of the bulbs. No correction was applied for the increase in volume in the first bulb, due to the compression of mercury and glass, since the order of accuracy required was less than 1 in 1000.



Explosion of Gases.

The explosive mixture was fired by the fusion of thin iron wire placed across the terminals in the centre of the bomb. Occasionally loss of gas occurred on explosion, which was detected by the smell of hydrocyanic acid. The joint, however, tightened up immediately and held a vacuum after the experiment. The bomb was distinctly warm to the hand after the explosion, and a

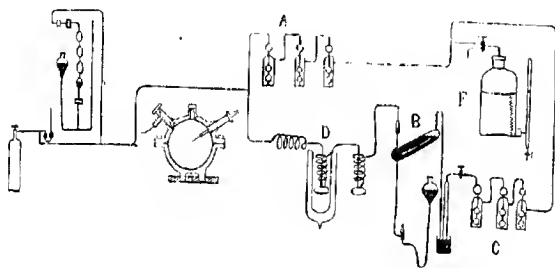
marked difference in the temperature of the thin metal parts was observed in experiments on the explosion of pure acetylene and that of a mixture containing 20 per cent. of nitrogen.

This behaviour would be explained by different rates of burning of the acetylene and nitrogen mixture. In experiment XIV, with 14 per cent. of nitrogen, it is evident that the explosion was incomplete.

Analysis and Measurement of Volume of Gases.

On account of the loss of gas (0.5 per cent.), the volume of the gases was measured after the explosion. The gases were led through bubblers (*A*, Fig. 2) to remove hydrocyanic acid and ammonia, into a large aspirator, *F*, fitted with a water manometer. The pressure in the aspirator was maintained at atmospheric, throughout, and the volume of the gases was measured by a determination of the water displaced. The first litre of gas, containing air from the bubblers, was measured and rejected. The remainder of the gas was collected in the aspirator and a portion analysed as a check. Some acetylene dissolved in the water, and the percentage of this gas was therefore low. For comparison, a sample was taken

FIG. 2.



directly from the bomb after the pressure had fallen to two atmospheres, and except for the slight difference due to the removal of a portion of acetylene in the first sample, the two analyses were in good agreement.

The gases in the bomb were dealt with in this way at pressures from three down to one atmosphere. From this point they were removed by means of a Toepler pump, *B*. On account of the small amount of water present, it was important to eliminate the hydrocyanic acid, ammonia, and water by means of liquid air, *D*, before passing the gases through the pump. The latter were collected at the base of the pump and transmitted through the bubblers, *C*, containing dilute acid and alkali, to the aspirator.

The total volume of the gases obtained in this manner, corrected for the vapour pressure of water and reduced to N.T.P., was used in calculating the percentages of ammonia and hydrocyanic acid.

The evacuation was carried out down to 2–3 mm., dry air admitted, and the bomb further evacuated. This was done as a

precaution, but the quantities of hydrocyanic acid removed at this stage were negligible.

The gases condensed in *D* were evaporated into the bubblers, *A*, and the solutions in *C* added to the respective solutions in *A*. The amounts trapped in *C* were negligible, showing that the whole of the hydrocyanic acid had been removed by liquid air.

The connecting tubes were all glass except where joined to the metal tube from the bomb by a short length of rubber tubing.

Hydrocyanic Acid and Ammonia.

It was found that hydrocyanic acid could be estimated by distillation from 0.5 per cent. sulphuric acid solutions without appreciable hydrolysis. The gases could thus be absorbed in a series of bubblers, *A*, containing normal acid and dilute alkali. The acid solution containing hydrocyanic acid was then distilled into alkali and the whole of the hydrocyanic acid solutions were combined. The ammonia was estimated in the usual manner; the back-titration method gave the same result as the direct method. The hydrocyanic acid was estimated by (*a*) silver nitrate with potassium iodide as indicator (Denige, "Classen," Anal. Chem. p. 675), and (*b*) iodometrically (Fordos and Gélis, *J. Pharm. Chim.*, 1853, [iii], 23, 48). The result obtained in (*a*) was usually 0.5 per cent. higher than that in (*b*); the mean value was taken.

The possibility of the loss of hydrocyanic acid by combination with the metal of the bomb must not be overlooked, but from the ease with which the results were reproduced (these are independent of the time the gases remain in the bomb) it appears that no appreciable action has occurred. Also, the interior of the bomb was as bright at the conclusion of these experiments as at the beginning. It was anticipated that the liquid hydrocyanic acid collected in the liquid-air tubes would show some tendency to polymerisation, but this was not found to be the case.

The carbon residue was analysed for hydrocyanic acid and ammonia, but these two gases were not present.

Permanent Gases.

The acetylene, hydrogen, and nitrogen in the residual gases were estimated in a constant-volume apparatus. Some difficulty was experienced in estimating the nitrogen with sufficient accuracy by the explosion method. In the later experiments, however, after the removal of the acetylene, the hydrogen was absorbed over copper oxide in a quartz tube, pure carbon dioxide being used to

wash out the tube and to drive the gas into the measuring apparatus. The percentage of nitrogen was in good agreement with the calculated value (Table II). A little carbon monoxide could be detected in some of the experiments. Benzene and other condensed substances could only have been present in small amounts.

Discussion of Results.

The experimental data are given in Tables I and II, the Roman numerals indicating the order in which the experiments were performed. The results of all the experiments are given.

TABLE I.

No. of expt.	Initial temp.	Initial per- centage of N.	Initial pressure in atm.	Final pressure in atm.	C.c. of HCN.	C.c. of NH ₃ .	Total volume of gases in c.c.
II	13°	2.97	3.21	3.05	(168.7)	(7.3)	12180
XIII	—	3.12	—	3.24	203.6	14.2	12940
I	13	3.15	3.22	3.05	(123.0)	(4.0)	12180
III	14	3.29	3.24	3.10	(188.9)	(8.0)	12400
XI	16	5.29	3.24	3.27	282.8	18.7	13090
VII	13.0	5.71	3.22	3.25	284.9	16.3	13000
V	10	9.66	3.26	3.16	340.1	16.8	—
VIII	14	9.71	3.33	3.29	356.0	17.7	13240
VI	12	10.44	3.26	3.33	362.7	20.6	13310
IV	12.5	12.06	3.20	3.19	371.4	—	12750
IX	14	12.88	—	3.09	360.3	18.3	12370
XIV	—	14.27	—	3.24	360.3	20.3	12950
X	15.5	18.04	3.26	3.10	381.0	20.5	12410
XII	18	22.05	3.01	2.95	388.2	16.9	12010

The first three experiments I, II, and III may be disregarded, as in these cases the methods of analysis had not been completely worked out. With two exceptions the pressures of the mixed gases lie between 3.21 and 3.26 atmospheres. It will be observed that the volume of the hydrocyanic acid increases with the quantity of nitrogen in the gases, whereas the ammonia is almost constant throughout. The volume of gases given in the last column of Table I includes the hydrocyanic acid and ammonia.

The carbon deposited in the bomb was removed, mixed with copper oxide, and heated in a stream of carbon dioxide, and the amount of nitrogen present was determined. The volume of the nitrogen which was fixed on the surface of the carbon was certainly less than 1 c.c., that is, less than 0.01 per cent. of the total gas.

Since the main chemical reactions, during the explosion and the cooling of the gases, are not accompanied by any change in the number of molecules of gas, the initial and the final pressures should be the same. The values in the fourth and the fifth columns

TABLE II.
Percentage Composition of the Residual Gases.

No. of expt.	N ₂		H ₂		HCN.	NH ₃ .	C ₂ H ₂
	Cale.	Obs.	Cale.	Obs.			
II	2.25	(2.39)	93.6	(93.4)	1.38	0.060	2.76
XIII	2.28	2.41	94.1	94.0	1.57	0.110	1.93
I	2.63	—	94.2	—	1.01	0.033	2.19
III	2.49	(2.77)	93.4	(93.1)	1.52	0.065	2.34
XI	4.13	4.34	91.2	91.0	2.17	0.143	2.48
VII	4.55	(4.67)	91.3	(91.2)	2.19	0.125	1.78
V	8.25	(8.55)	86.3	(86.0)	2.69	0.133	2.63
VIII	8.28	(8.43)*	86.8	86.7*	2.72	0.135	2.11
VI	9.00	(9.32)	85.8	(85.5)	2.73	0.154	2.29
IV	10.61	(10.81)	83.4	(83.7)	2.91	—	2.56
IX	11.34	(11.49)	83.5	(83.3)	2.92	0.148	2.12
XIV	12.80	12.46	78.7	79.0	2.78	0.157	5.53
X	16.42	—	78.1	—	3.07	0.165	2.24
XII	20.33	19.92	74.3	74.7	3.24	0.141	1.96

* Hydrogen estimated by the palladium method; the other values in brackets were obtained by the explosion method.

TABLE III.

No. of expt.	N ₂ (Calc.)	[NH ₃]	[NH ₃]	[HCN] ²	[HCN]
		[HCN]	[H ₂][HCN]	[H ₂][N ₂]	[H ₂][N ₂] ¹
XIII	2.28	0.070	0.00074	0.0115	0.0126
XI	4.13	0.066	0.00072	0.0125	0.0141
VII	4.55	0.057	0.00063	0.0116	0.0137
V	8.25	0.049	0.00057	0.0101	0.0142
VIII	8.28	0.050	0.00057	0.0103	0.0143
VI	9.00	0.057	0.00068	0.0097	0.0141
IV	10.61	—	—	0.0095	0.0145
IX	11.34	0.051	0.00061	0.0099	0.0143
XIV	12.80	0.057	0.00072	0.0077	0.0138
X	16.42	0.053	0.00068	0.0074	0.0140
XII	20.33	0.044	0.00059	0.0069	0.0143

(Table I) show the degree of correspondence between the initial and the final pressures measured at 0°. In general, the final pressures are somewhat lower, except in experiment VI, where it is possible that a leak of air inwards occurred during the measurement. The difference between the values is due, as previously mentioned, to the leak of gas at the moment of explosion.

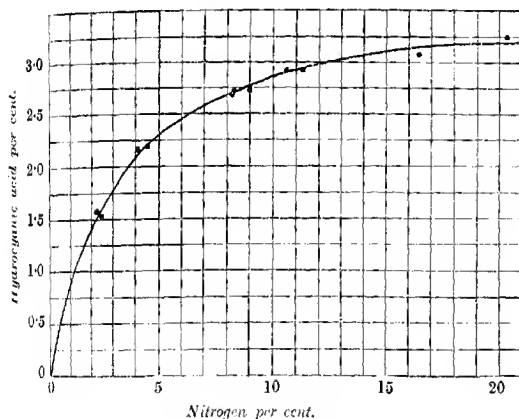
In Table II is given the percentage composition of the residual gases. The nitrogen and hydrogen figures, columns 2 and 4, are obtained by difference, and these may be compared with the experimental figures in the next columns. The agreement is within experimental error. The explosion method of estimating hydrogen was not sufficiently accurate, many results being necessary to

obtain the average value given in the tables; consistent results were obtained only by burning the hydrogen with oxygen over palladium or alone over copper oxide.

In order to arrive at the gas reaction constants in Table III, the calculated percentages of hydrogen and nitrogen have been employed.

In Fig. 3 the percentage of hydrocyanic acid is plotted against residual nitrogen. A smooth curve is obtained, which suggests a logarithmic relationship, possibly due to adsorption phenomena. The ammonia is almost constant throughout. The acetylene in the residual gases varies irregularly between 1.15 and 2.76 per cent.

FIG. 3.

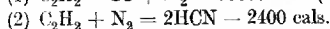
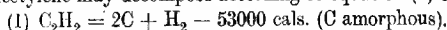


except in experiment XIV : 5.53 per cent.). As a small percentage of acetylene, in the neighbourhood of the walls and ignition plugs, must escape combustion, this irregularity is to be expected. In experiment XIV, however, explosion was less complete than usual. Similar percentages of acetylene are, however, frequently found in the gases from explosive processes, so that a portion of the acetylene in the above experiments is doubtless due to a combination of hydrogen and carbon at the high temperatures in the bomb.

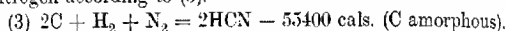
Conclusions.

The chemical reactions which occur during the explosion of a mixture of acetylene and nitrogen are rendered fairly clear by

Wartenberg's theoretical analysis of the possible reactions (*loc. cit.*). Acetylene may decompose according to equation (1) or (2):



The former is undoubtedly the principal reaction which occurs, for otherwise heat would not be liberated during the explosion. If this reaction goes to completion, and no dissociation of hydrogen occurs, it may be calculated that the temperature of explosion of pure acetylene is 3140° , whilst that of a mixture containing 10 per cent. of nitrogen is 3050° . In neither case can these temperatures be completely realised, for reaction (1) is reversible at high temperatures. This holds particularly for mixtures of nitrogen and acetylene, for not only can these substances react according to (2), but also the products of dissociation of acetylene will combine with nitrogen according to (3).



Both of these reactions take place with absorption of heat, so that the theoretical maximum of temperature is never reached.

At the temperature of explosion, therefore, the principal products will be carbon, hydrocyanic acid, acetylene, hydrogen, and nitrogen. During the process of cooling to room temperature, reaction (1) and the back reactions of (2) and (3) will take place, and the percentages of the gases in the cooled mixture will depend on the rate of cooling. The rate of cooling determines the "chilling interval" during which the chemical reactions are arrested, and we should expect the mixtures containing high percentages of nitrogen, on account of their slow rate of explosion, to be chilled at a lower temperature than nearly pure acetylene. It does not seem possible to decide between equations (2) and (3) from our results, though (3) gives a better constant. Wartenberg (Table IV) showed that the equilibrium constant of equation (3) decreased with decrease in temperature.

TABLE IV.

Temp.	K.
2148° abs.	0.0097
2025	0.0041
1908	0.00157.

It is found in our experiments that the relation $[\text{HCN}]^2/[\text{H}_2][\text{N}_2]$ varies from 0.0124 with 4.13 per cent. of nitrogen to 0.0069 with 20.33 per cent. of nitrogen. The former corresponds with the equilibrium constant at approximately 1950° , and the latter with that at 1800° , whence it appears that the reactants have been chilled at a lower temperature in the mixture containing 20 per

cent. of nitrogen. The effect of rate of cooling on the equilibrium constant is, however, much greater than in the case of the water-gas reaction (Andrew, T., 1914, **105**, 444), and the explanation of this perhaps lies in the nature of the heterogeneous reaction (3). The temperature coefficient of this reaction may be unusually large.

It is found that the empirical equation

$$\frac{[\text{HCN}]}{[\text{H}_2][\text{N}_2]^{0.37}} = \text{a constant} = 0.014$$

holds over the range 4 to 20 per cent. of nitrogen. No explanation of this relationship can be given at present.

At lower temperatures, in the neighbourhood of 1300° and 1000° respectively, reactions (4) (Bergmann, *J. Gasbeleucht.*, 1896, 117), and (5) may take place to an appreciable extent.

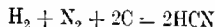
(4) $\text{HCN} + \text{H}_2 = \text{C} + \text{NH}_3 + 39800 \text{ cal. (C amorphous)}$.

(5) $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3 + 24100 \text{ cal.}$

The calculations in Table III show that $[\text{NH}_3]/[\text{H}_2][\text{HCN}]$ is a constant within the experimental error of the ammonia estimation, indicating that hydrocyanic acid is the source of the ammonia.

Summary.

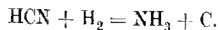
Mixtures of acetylene and nitrogen have been exploded at constant volume, and up to 3.24 per cent. of hydrocyanic acid has been found in the gases from the explosion. The results throw light upon the mode of production of hydrocyanic acid and ammonia in the cooling gases. The reaction constants for the equation



are found to vary between 0.0124 for 4.13 per cent., and 0.0069 for 20.33 per cent. of nitrogen in the residual gases, corresponding with a "chilling" temperature of 1950° and 1800° respectively.

The relation $\frac{[\text{HCN}]}{[\text{H}_2][\text{N}_2]^{0.37}} = 0.014$ has been found to hold for an explosion of mixtures of nitrogen and hydrogen at 3 atm. pressure in a closed vessel of 4 litres capacity.

The concentration of ammonia bears a close relation to the concentration of hydrocyanic acid, and it is probable that this gas is produced according to the equation



A new type of manometer is described for the measurement of pressures up to five atmospheres.

The authors are indebted to Professor F. G. Donnan for kindly

providing the facilities for this work, and to the Department of Scientific and Industrial Research for a grant for the purchase of the phosphor-bronze bomb.

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CCXIX.—*Physical Chemistry of the Oxides of Lead.*
Part II. The Supposed Enantiotropy of Lead Monoxide.

By SAMUEL GLASSTONE.

PREVIOUS authors (Dittc, *Compt. rend.*, 1882, **94**, 1310; Geuther, *Annalen*, 1883, **219**, 56; Ruer, *Zeitsch. anorg. Chem.*, 1906, **50**, 265; Germs, *Diss. Gröningen*, 1917) state that two enantiotropic forms of lead monoxide (red and yellow) must be clearly distinguished. Ruer (*loc. cit.*) suggested that the red (and reddish-brown) form of lead monoxide was stable at all temperatures below 620°, whereas the yellow form was stable only above this temperature. This suggestion was based on the fact that the red and the reddish-brown forms, if heated to 720° (at least) and 620° respectively and then allowed to cool, generate the yellow form. The reverse change could only be brought about by grinding, or by heating with concentrated (50 per cent.) alkali. The weak points in Ruer's arguments are (a) a cooling curve showed no break, (b) the red form had to be heated to a temperature 100° higher than the reddish-brown before it would give the yellow form on cooling, (c) a pressure of 2000 atmospheres would not change the yellow form to the reddish-brown; the grinding effect was necessary, (d) the reddish-brown form, either bought or obtained by grinding the yellow, was even more soluble in water than the original yellow, and (e) the change from the yellow to the red form had never been observed during very slow cooling from the supposed transition point downwards. Germs (*loc. cit.*), summarising previous work, emphasises the difference in colour, in density, and in solubility. As a result of his own heating experiments, he concludes that the transition point between red and yellow lead monoxide is 587°. The rate of change of the red to the yellow form is very slow at this point, but increases as the temperature rises. The brown forms (ground yellow) are said to be only partly changed to red, and therefore the

change back to yellow is rapid at 587° . Attempts to change the yellow to the red form below this temperature failed unless the former was brought into solution, for example, in molten potassium nitrate at 350° ; no mention is made of the possible formation of triplumbic tetroxide in this case.

By setting up half-elements of the type $\text{Pb}|\text{PbO } N\text{-NaOH}$, it is possible to determine the free energy of the reaction $2\text{PbO} = 2\text{Pb} + \text{O}_2$. With a transition point as high as 587° , the free energy change of this reaction at room temperature should be very different for the two forms; by repeating the determinations at other temperatures, the transition temperature might be found by extrapolation. Experimental determinations, however, led to no such appreciable differences at temperatures between 0° and 50° . Any small differences that were found, as well as the differences in physical properties (except perhaps density) mentioned by Ruer and by Germs, may be readily explained on the ground of differing states of division or agglomeration. Evidence for this view is brought forward, and explanations for the properties of the various forms of lead monoxide are developed.

EXPERIMENTAL.

The various forms of lead monoxide and *N*-sodium hydroxide free from carbonate were prepared as described in Part I (this vol., p. 1689).

Lead Electrodes.—Based upon previous work by Getman (*J. Amer. Chem. Soc.*, 1916, **38**, 792), Lewis and Brighton (*ibid.*, 1917, **39**, 1906), Günther (*Zeitsch. Elektrochem.*, 1917, **23**, 197), and Krahmer (*ibid.*, 1920, **26**, 97), the conclusion was drawn that in order to produce satisfactory lead electrodes the following points were to be noted: (a) electro-deposition with the use of a very small current density would give gradual and even deposition and thus avoid surface strains, (b) the use of an "addition agent" (Mathers and McKinney, *Trans. Amer. Electrochem. Soc.*, 1915, **27**, 131) would probably produce an even deposit, and (c) a greyish-white, microcrystalline deposit was desirable.

Ten grams of powdered Barbadoes aloes were extracted with 250 c.c. of hot water by shaking and filtering. The solid residue was roughly dried and used as the "addition agent." The bath was made up from 100 c.c. of water, 10 grams of pure lead nitrate, and 1 gram of aloes residue dissolved in 5 c.c. of glacial acetic acid. Two anodes of Kahlbaum's lead were wrapped in filter paper and suspended in the solution. The cathode, placed between the two anodes, consisted of 1 sq. cm. of platinum foil, roughened by sand paper to aid the deposit in sticking. An *E.M.F.* of 2 volts was

applied and a current of 4 milliamperes (current density of 2×10^3 amps./cm.²) passed for two hours. The cathode was then removed, well washed with recently boiled water, and immediately used in the electrode vessels. The deposit of lead was smooth and micro-crystalline, of a light grey colour, and adhered well to the platinum.

Measurements.

Electrode vessels of simple type were used; they consisted of tubes 10 cm. long and 2 cm. wide, closed at the bottom and fitted with side tube and tap. The various forms of lead monoxide were filled into these vessels to a depth sufficient completely to cover the lead; the electrode solution (*N*-sodium hydroxide) was poured in and finally the lead electrode with its glass tube was inserted and gently forced in so as to leave no air in the vessel. In order to avoid the difficulty of diffusion potential, the potential of the lead half-element was measured against that of the $\text{Hg}|\text{HgO } N\text{-NaOH}$ half-element, accurately defined by Donnan and Allmand (T., 1911, **99**, 845), the same solution of sodium hydroxide being used in both half-elements and also in the connecting vessel. The *E.M.F.* of this combination was measured in series with and against a standard Weston cell, a metre bridge and capillary electrometer being used for the preliminary measurements at room temperature. After measurements were taken, the lead electrode vessels were attached to the spokes of a wheel revolving twenty-four times every minute, so as to get gentle yet efficient shaking. The vessels were removed from day to day, and the potentials measured until constant and steady values were obtained.

Results.

Scale $\text{H}_2|\text{N-H} = 0$. Measurements at room temperature (20°).

P.D. of $\text{Hg}|\text{HgO } N\text{-NaOH} = 0.1140$ volt at 20°.

Form of lead monoxide.*	Time after setting up (in days).				
	0	1	2	3	4
1. Reddish-brown	-0.558 -0.559				-0.559
2. Yellowish-green	-0.561 -0.559				-0.559
3. Red	-0.552 -0.553	-0.559 -0.558	-0.559		-0.559 -0.560
4. R. B. by KOH	-0.555	-0.555		-0.559	-0.560
5. Y. G. by KOH	-0.553 -0.554	-0.553 -0.559		-0.559	-0.559 -0.560
6. Yellow	-0.558	-0.559		-0.560	-0.560
7. Commercial	-0.552			-0.558	-0.558
8. Ground	-0.554			-0.559	-0.560

* For the description of these forms see this vol., p. 1690.

Results (continued).

Scale $H_2/N.H^* = 0$. Measurements at room temperature (20°).

P.D. of $Hg|HgO\ N-NaOH = 0.1140$ volt at 20° .

Form of lead monoxide.*	Time after setting up (in days).					Final.
	6	7	8	9	10	
1. Reddish-brown		-0.559	-0.559	-0.559	-0.559	-0.558
2. Yellowish-green		-0.559				-0.559
		-0.559			-0.558	-0.558
3. Red		-0.558	-0.558			-0.558
				-0.560		-0.560
4. R. B. by KOH		-0.560				-0.560
5. Y. G. by KOH						-0.558
						-0.550
6. Yellow	-0.560					-0.550
7. Commercial ...	-0.559			-0.559		-0.559
8. Ground						-0.560
	Mean	-0.559 volt.

* For the description of these forms see this vol., p. 1690.

Cumming (*Trans. Faraday Soc.*, 1907, 2, 199) obtained a value of -0.539 volt for the potential of the half-element $Pb|PbO$ (yellow) $N-NaOH$ at 25° , without correcting for the diffusion potential between N -sodium hydroxide and N -potassium chloride solutions. The Henderson formula being used, this potential is calculated as $+0.19$ volt, the sodium hydroxide side being positive. The potential of the half-element alone is thus -0.558 volt. The agreement with the result given above is satisfactory.

Discussion of Results.

Almost all the electrodes developed initial potentials up to 3 millivolts more positive than the final values, and within two or three days the different forms of lead monoxide had become adjusted to give an almost identical value in each case.

The initial high values may be due to two causes: (a) a metastable form of lead monoxide, being more soluble, would give higher initial values, which would diminish as this form disappeared, and (b) the higher initial solubility of small particles. In the first case the metastable form could be present only in very small amount, as in no instance was any alteration of the solid lead monoxide noted when the steady state was reached. The second possibility is in excellent agreement with the facts mentioned in Part I (*loc. cit.*). Almost every form of lead monoxide contains a number of very small particles having a solubility of about 0.054 gram-mol. per litre. Even the red form contains some of these particles, as can be shown by shaking a large amount of this form with a small quantity of N -sodium hydroxide solution; in this

way a value of 0.055 gram-mol. of dissolved lead monoxide per litre has been obtained. The normally saturated solution of lead monoxide in *N*-sodium hydroxide contains 0.035 gram-mol. per litre. Substituting these two values in the ordinary formula for a concentration cell with bivalent ions, we find that the difference between the initial and the normal solubility corresponds with a potential of 5.5 millivolts, in agreement with the value actually found (6 millivolts).

The fact that all the forms of lead monoxide examined gave almost identical values for the final potential, shows that the free energy of the reaction, $2\text{PbO} = 2\text{Pb} + \text{O}_2$, is almost independent of the form of lead monoxide used. With the transition point of 587° suggested by Germs (*loc. cit.*), we should expect considerable differences in the free energy at the low temperature of 20° . The fact that negligible values were obtained, which could be explained on the grounds of experimental error and slight differences in solubility, is evidence in favour of a purely physical explanation for the differences between the various forms of lead monoxide.

The question of differences of free energy was further investigated at 0° and 50° , by setting up cells of the type $\text{Pb}|\text{PbO (A)} \text{ } N\text{-NaOH} \text{ } \text{PbO (B)}|\text{Pb}$, where A and B represent the various forms of lead monoxide in turn, and measuring their *E.M.F.*'s in series with and against a Weston cell. Slight fluctuations from the normal value of the standard cell were noted, which could be explained only on the grounds of error of experiment.

Solubility and Potential Values.

Although the potentials of the half-elements $\text{Pb}|\text{PbO } N\text{-NaOH}$ had become adjusted to almost identical values, yet the main bulk of the electrode solutions varied in concentration from 0.049 to 0.029 gram-mol. of lead monoxide per litre (see this vol., p. 1602). This appears to be contradictory at first sight; the concentration that fixes the potential of the half-element, however, is that of the infinitely thin layer of solution actually in contact with the lead of the electrode. The latter is completely surrounded by a depolariser (lead monoxide) and equilibrium therefore sets in very rapidly at this point, thus giving normal potential values, although the main solution may be unsaturated or supersaturated. It has previously been shown that the solubility of the various forms of lead monoxide tends towards the same value, and we should therefore expect the same tendency in the potential of the alkaline lead-lead monoxide half-element. The difference in the solubility of the red and the yellow forms, namely, 0.035 and 0.039 gram-mol. per litre, would lead to a potential difference of 1.5 millivolts.

Definitive Measurements.

In order accurately to define the Pb|PbO *N*-NaOH half-element, to detect such differences as given above, and to find the temperature coefficient of the half-element, *P.D.* determinations were made with a Kelvin and Varley vernier potentiometer (Paul) reading to 0.0001 volt. Constant temperatures were obtained by means of a thermostat at 25.0° and a large vessel of melting ice at 0°.

The following results were obtained five weeks after setting up the electrodes, by which time the values had become quite constant.

Pb|PbO *N*-NaOH.

Yellow Form (Product No. 2).

	25°	0°
—	0.5597 volt.	— 0.5512 volt.
—	0.5598 "	— 0.5514 "
—	0.5599 "	— 0.5514 "
—	0.5597 "	— 0.5512 "
Mean	— 0.5598 "	Mean — 0.5513 "

The temperature coefficient is — 0.00034 volt/degree.

Red Form (Product No. 3).

—	0.5619 volt.	— 0.5537 volt.
—	0.5620 "	— 0.5536 "
—	0.5623 "	— 0.5542 "
—	0.5621 "	— 0.5535 "
Mean	— 0.5621 "	Mean — 0.5537 " (value * omitted)

The temperature coefficient is — 0.000336 volt/degree.

In order to obtain reproducible results two conditions are necessary: (1) the lead electrode must be completely covered by the polariser, and (2) the latter should not be disturbed in any way, so that true equilibrium may be established. Vessels of the type used for the Hg|HgO half-element are recommended.

The Effect of Carbonate.

(a) *In the Alkali.*—So far as was investigated, sodium carbonate in quantities up to 3.0 grams per litre had no effect on the *P.D.* of the Pb|PbO electrode (see also p. 1924).

(b) *In the Lead Monoxide.*—The effect in this case was to give such higher initial values, for example, — 0.550 volt, which only very gradually diminished in the course of a month. In order to get reproducible half-elements, the lead monoxide used must be free from carbonate.

Density Determinations.

Germers (*loc. cit.*) emphasises the fact that the yellow forms of lead monoxide always have a higher density than the red. From

the many values given by Dammer ("Anorganische Chemie," II, (2), pp. 520 *et seq.*) it appears that the density of any form depends on its method of preparation (compare Ditte, *loc. cit.*), and that some forms of the yellow oxide have densities even lower than that of the red. A series of experimental determinations, care being taken to avoid occluded air, confirmed this conclusion.

Density at 20° compared with the density of water at 4°.

Colour.	Preparation.	Density.
(i) Red.	Product No. 3.	9.28
(ii) Reddish-brown.	Product No. 1.	9.23
(iii) Yellow.	5% boiling NaOH on Pb(OH) ₂	9.26
(iv) " "	10% " " " "	9.39
(v) Yellowish-green.	20% " " " "	9.52
(vi) Yellow.	NH ₄ OH on boiling basic acetate.	9.41
(vii) " "	Commercial oxide, heated.	9.20
(viii) " "	Product No. 1, heated.	9.53
(ix) Reddish-brown.	No. viii, ground.	9.33
(x) Yellow.	No. ix, reheated.	9.51

On the whole, no definite conclusions can be drawn from density measurements; we may compare the case of magnesium oxide, where the density is found to depend on the previous history of the specimen (Parravano and Mazzetti, *Atti R. Accad. Lincei*, 1921, [v], 30, i, 63).

*Heating Experiments.**

The results are summarised below.

(1) The temperature to which any red form required to be heated in order to give the yellow form on cooling depended on the state of division. The large red particles changed rapidly at 630° (very slowly at 600—630°); the reddish-brown form (wet method) changed at 600°; the brown powders made by grinding the red form changed from 540° upwards, the temperature depending on the state of division. The supposed transition point of Germs (*loc. cit.*) is 587°.

(2) The brown-forms made by very finely grinding various specimens of the yellow, required to be heated only to 540° in order to give the yellow form on cooling. This temperature, so very different from that of Ruer (620°) and that of Germs (587°), may like the density (see above), depend on the particular form of yellow oxide used in the first place.

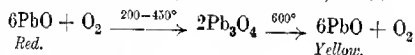
(3) Keeping the red form at 540° for four hours produced no visible change in colour. These results render invalid some of the conclusions of Germs (*loc. cit.*).

* All temperatures were checked by means of a platinum resistance thermometer.

There appear to be two possible transition temperatures: (a) 500–600°, the minimum temperature necessary to give the yellow form on cooling, and (b) 350°, where the yellow colour first appears. A cooling curve should show a break in the vicinity of a transition point. A porous pot was half filled with about 300 grams of pure commercial lead monoxide and fixed vertically in an electric furnace. A thermo-electric junction was thrust well into the oxide and the whole heated to 700°. The current was then switched off and readings of temperature and time taken while the furnace cooled to 160° in three hours. No break could be detected in the region of 600° or at 350°, the curve being quite smooth along the whole of its length.

It was noted that the yellow oxide in the pot at the end of the experiment was in the form of a block, in spite of the fact that no obvious fusion had taken place and the original substance had been put in as a powder. The importance of this observation will appear later.

Since triplumbic tetroxide, on heating, always gives the yellow form of lead monoxide, it appeared possible that the production of the latter from the red form of lead monoxide was due to the intermediate formation of triplumbic tetroxide, thus:



This suggestion was tested in two ways: (a) the electric furnace was heated to 600°, and a sample of the reddish-brown oxide put in; the rapid heating to 600°, at which temperature triplumbic tetroxide is completely dissociated in air, should prevent appreciable oxidation. On cooling, however, the product was yellow.

(b) The red and the reddish-brown oxides were heated in a current of pure nitrogen; on cooling, the colour of both specimens was yellow. These experiments proved that the colour change was not due to the intermediate formation of triplumbic tetroxide.

Crystalline Form.

There appears to be some confusion on this point. Nordenskiöld (*Pogg. Ann.*, 1861, **114**, 619) found the axial ratios of crystals of yellow lead monoxide to be 1:0.6706:0.9764; he therefore concluded that the crystals were rhombic. If the ratios had been 1:0.6706:1 (within the limits of error), the crystals would have been tetragonal. Lüdecke, in Geuther's paper (*loc. cit.*), states that the crystal diagram of the red form of lead monoxide resembles that given for the yellow form by Nordenskiöld, but by examination of the former in polarised light concludes that the crystal is tetra-

gonal. The possibility of both red and yellow forms having the same crystalline structure is obvious. Within recent years, two observers have examined natural lead monoxide; Scott (*Min. Mag.*, 1914, 17, 143) states that this substance is red with a yellowish-brown streak and that its optical characteristics suggest orthorhombic symmetry, and Larsen (*Amer. Min.*, 1917, 2, 18) states that the central portion of the plates of natural lead monoxide consists of the yellow, orthorhombic modification, and the borders of the red, tetragonal modification. At the request of the author, Mr. J. E. Barnard kindly examined specimens of the red, reddish-brown, yellow, and yellowish-green forms of lead monoxide. He reports that the latter two forms are certainly agglomerates, and that in every case the ultimate constituent crystals appear to be identical (tetragonal) or closely allied.

The Agglomerate Theory.

All the evidence so far given is in favour of the view that the differences between the various forms of lead monoxide are attributable merely to the state of physical division. The red form, on grinding, gives brownish-yellow particles, the change of colour being due to increased reflection of white light, and it is here suggested that these brownish-yellow particles, when agglomerated, are yellow or greenish-yellow, because the agglomerates, on gentle pressure with a spatula or rubbing between paper with the fingers, give brown particles. A striking experiment in favour of this view is the following. Lead hydroxide of the formula $3\text{PbO}\cdot\text{H}_2\text{O}$ can be prepared in comparatively large crystals (1 mm. in diameter). When these crystals are heated, yellow lead monoxide is obtained, the shape of the original crystals being retained, but when the crystals are first ground and then heated, the resulting lead monoxide is reddish-brown.

Explanation of the Variation of Colour.

It is suggested that all forms of lead monoxide reflect green light and transmit red, the violet end of the spectrum being absorbed. In the case of the yellow and the green agglomerates, owing to the enormous number of internal surfaces, the red light is lost by internal reflection (and eventual absorption), and therefore only the green colour is visible. With a smaller loss of red light the yellowness would increase, whilst the larger agglomerates would be more green in colour. In the microscopic examination, the transmitted red light could occasionally be seen. A very similar case to the one under discussion occurs during the precipitation

of gold sols. These sols contain green particles which, on agglomerating, appear brown; the particles here probably transmit green light and reflect red, and therefore give in the reverse order the effects displayed by lead monoxide.

Changes on Heating.

The theory is proposed that when the comparatively large crystals of red lead monoxide are heated, splintering into smaller particles takes place at some temperature (600—650°), possibly due to unequal expansion in different directions. These smaller particles still adhere together on cooling and in this way form the yellow agglomerates of brown particles. When the agglomerates are crushed, the constituent brown particles become visible.

In the case of the reddish-brown or brown forms, at a certain temperature (540—600°) the very fine particles fuse; thus a large number of small particles join together and agglomerate on cooling by the process of sintering. Confirmation of this view is found in the fact noted on p. 1921, that powdered lead monoxide, heated to 700°, is recovered on cooling in the form of a yellow block. Reinders and Hamburger (*Zeitsch. anorg. Chem.*, 1914, 89, 71) state that the available surface of yellow lead monoxide decreases on heating owing to the particles sintering together. The temperature at which sintering takes place depends of course on the size of the particles, and in this fact is found the explanation of the variation in the temperature to which the different forms have to be heated in order that they shall give the yellow form on cooling (p. 1920). (The melting point of lead monoxide is given in Watt's Dictionary of Chemistry, 1892, as 585—630°; the latest value, given by Germs [*loc. cit.*] and others, is 875°.)

These assumptions account for the different temperatures at which the conversion of the red form, and of the series of brown and yellowish-brown powders made by grinding this form, into the yellow variety occurs. The irreversibility of the change from the yellow to the red form by slow cooling (compare Germs, *loc. cit.*; Ruer, *loc. cit.*) is obvious; dissolution is an essential, intermediate step.

These suggestions offer explanations of the properties of the various forms of lead monoxide on purely physical grounds, without involving enantiotropic changes.

The Solubility Product of Lead Monoxide at 25°.

Using the value — 0.562 volt as the potential of the Pb|PbO (red) | NaOH electrode, and — 0.130 volt as the normal electrode potential

of lead at 25° (Lewis and Brighton, *loc. cit.*; Getman, *J. Amer. Chem. Soc.*, 1918, 40, 611), we obtained 2.27×10^{-15} gram-ion per litre as the concentration of lead ions in *N*-sodium hydroxide saturated with red lead monoxide. The hydroxyl-ion concentration in this solution is 0.72 gram-ion per litre. The solubility product of lead monoxide is thus given by

$$L = [\text{Pb}^{++}][\text{OH}]^2 = 2.27 \times 10^{-15} \times 0.72 \times 0.72 = 1.17 \times 10^{-15}.$$

The concentration of lead ions in a solution of lead monoxide in water is approximately $\sqrt[3]{L}$, that is, about 0.66×10^{-5} gram-ion per litre. The solubility of red lead monoxide in water is 0.26×10^3 gram-mol. per litre. This rough comparison emphasises the uncertainty of the ionisation of lead monoxide in water, and the futility of determining the solubility of lead monoxide or hydroxide in water by the conductivity method (compare Pleissner, *Arch. Kaiser. Gesundh.-Amt.*, 1907, 26, 384).

The Effect of Carbonate.

In order to alter the potential of the alkaline lead electrode, the addition of carbonate must affect the concentration of the lead ions, by being present in an amount sufficient to make the product of $[\text{Pb}^{++}]$ and $[\text{CO}_3^{--}]$ exceed the solubility product of lead carbonate, which is 3.3×10^{-14} (Pleissner, *loc. cit.*). To reach the solubility product of lead carbonate, the CO_3^{--} concentration must be $\frac{3.3 \times 10^{-14}}{2.3 \times 10^{-15}}$, that is, 14 gram-ions per litre, which is, of course, impossible under the conditions of working. Assuming, as we have done, that the carbonate does not affect the concentration of hydroxyl ions, it will have no appreciable effect on the potential of the $\text{Pb}|\text{PbO } N\text{-NaOH}$ electrode.

Dissociation Pressures.

The cell $\text{Pb}|\text{PbO } N\text{-NaOH } \text{H}_2$ (1 atm.)|Pt, whose *E.M.F.* is $-0.562 - (-0.809) = 0.247$ volt, may be regarded as an $\text{H}_2 - \text{O}_2$ cell, with oxygen supplied at the dissociation pressure of the reaction $2\text{PbO} \rightarrow 2\text{Pb} + \text{O}_2$, at 25°. Using the value 1.226 volts as the *E.M.F.* of the $\text{H}_2 - \text{O}_2$ cell with both gases at atmospheric pressure at 25°, and substituting the values in the formula connecting the *E.M.F.* of these gas cells with the pressure of the gases, we find that the dissociation pressure of oxygen produced by the decomposition of red lead monoxide at 25° is 4.2×10^{-67} atm.

By the use of Nernst's theorem, the dissociation pressure can be

calculated when it is known that the heat absorbed in the dissociation is 100,600 calories per gram-mol. of oxygen (Thomsen); the result obtained is 1.9×10^{-67} atm. at 25° . Considering the low order of magnitude of these values, the agreement is satisfactory.

The temperature at which the dissociation pressure in the above reaction is equal to 0.21 atm. is the temperature at which lead monoxide will decompose completely if heated in air. This temperature can be calculated by three methods, it being assumed that both lead monoxide and lead remain solid.

Method 1.—If the cells $\text{Pb}|\text{PbO alkali H}_2|\text{Pt}$ and H_2 (1 atm.) — H_2 (0.21 atm.) are imagined to have their temperature raised until both have the same *E.M.F.*, we know that at this temperature lead monoxide will have a dissociation pressure of 0.21 atm. The *E.M.F.* of both these cells is known at 25° , and their temperature coefficients may be calculated by applying the Gibbs-Helmholtz equation to the known heats of reaction. Assuming that these coefficients remain constant over a considerable range of temperature, we find that the *E.M.F.*'s would become equal at 2600° abs. At this temperature lead monoxide would completely decompose if heated in air.

Method 2.—Using the integrated form of the van't Hoff isochore, where partial pressures are involved, we get $R \log_e K_p = -\frac{Q_p}{T} + C$, where Q_p is the heat absorbed, and C is an integration constant. The latter can be evaluated as follows. If the ratio of the concentrations of lead monoxide and lead can be considered constant at all temperatures, we can replace K_p in the above expression by p_{O_2} at any temperature. For 298° abs. we have found that p_{O_2} is equal to 4.2×10^{-67} , and taking Q_p as 100,600 cal., we obtain $C = 32.0$. Assuming that Q_p remains constant, it is found that p_{O_2} is equal to 0.21 atm. at 2860° abs.

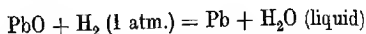
Method 3.—Stahl (*Metallurgie*, 1907, 4, 682), using Nernst's formula, has calculated that the temperature at which the pressure of oxygen in the system under discussion becomes equal to 0.21 atm. is 2348° abs.

Considering the approximations involved in connexion with the pressures of lead monoxide and lead, and with the various heats of reaction, the agreement between the three methods is good.

Heat of the Reaction $\text{Pb} + \frac{1}{2}\text{O}_2$ (1 atm.) = PbO at 25° .

This value can be calculated from electrochemical data by the use of the Gibbs-Helmholtz equation. The *E.M.F.* of the cell $\text{Pb}|\text{PbO (red)}|\text{N-NaOH H}_2|\text{Pt}$ is 0.2469 volt at 25° , and 0.2603

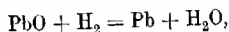
volt at 0° (from the known potentials of the two electrodes). The temperature coefficient is thus -0.00054 volt/degree. The total energy of the reaction



at room temperature is then calculated as 18,790 cal. Taking the heat of formation of liquid water as 68,400 cal., we obtain 49,610 cal. as the heat of formation of red lead monoxide at room temperature. The thermochemical value (Thomsen) 50,300 cal. the form of lead monoxide not being stated, is probably less accurate than the electrochemical value.

Calculation of E.M.F. by Nernst's Theorem.

Using the method of Nernst (*Sitzungsber. K. Akad. Wiss. Berlin*, 1909, 247), it is possible to calculate the *E.M.F.* of the cell $\text{Pb}|\text{PbO} - \text{H}_2|\text{Pt}$ at 0° . The reaction involved is



the water being in the form of ice. For this reaction at 17° , we have :

$$Q_T = 68,400 (\text{H}_2\text{O}) + 1580 (\text{ice, water at } 17^\circ) - 50,300 (\text{PbO}) = 19,680 \text{ cal.}$$

The molecular heats of reactants and resultants are taken as 11.5 for lead monoxide, 6.8 for hydrogen, 6.4 for lead, and 9.5 for ice. The difference between the molecular heats of the reactants and of the resultants is 2.7 cal., leading to a value of -0.0014 for β (Nernst, *loc. cit.*), and thus $Q_0 = 18,783$ cal. Assuming that the "chemical constant" for hydrogen is 1.6, we obtain the figure 0.251 volt as the *E.M.F.* of the above cell at 0° . The experimental value is 0.260 volt at 0° , with water instead of ice as one of the products of the reaction. The heat of formation of lead monoxide being taken as 49,610 cal. (see above), the *E.M.F.* is calculated as 0.265 volt.

Using a more approximate method in which water is involved instead of ice, we get $Q_T = 18,100$, $\beta = -0.016$, and Q_0 is then 18,430. The value for the *E.M.F.* of the cell at 25° is then 0.25 volt, the actual experimental value being 0.247 volt.

Summary.

(1) The results of measurements of the $\text{Pb}|\text{PbO} \text{ N-NaOH}$ potential are not in harmony with the theory that lead monoxide is enantiotropic.

(2) The temperature to which the red form of lead monoxide has to be heated in order to give the yellow form on cooling, depends on the state of division of the former.

(3) Crystallographic evidence is shown to be very confusing.

(4) The difference in properties of the various forms of lead monoxide is explained on the grounds of degree of sub-division or agglomeration.

(5) The solubility product of red lead monoxide is 1.17×10^{-15} at 25°.

(6) The dissociation pressures of oxygen derived from lead monoxide are calculated by various methods which give good agreement.

(7) The heat of formation of red lead monoxide is 49,610 calories.

(8) The *E.M.F.*'s calculated by Nernst's theorem are in good agreement with the experimental values.

The author desires to thank Professor Alluand for suggesting the work and for criticism and advice, and also Mr. J. E. Barnard for kindly undertaking the crystallographic examination of the various forms of lead oxide.

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CCXX.—*Investigations into the Analytical Chemistry of Tantalum, Columbium, and their Mineral Associates. I. The Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates. II. The Separation of Zirconium from Tantalum and from Columbium.*

By WALTER RAYMOND SCHOELLER and ALAN RICHARD POWELL.

ONE of the most difficult problems that confront the mineralogist is the analysis of the tantalum- and titano-columbates. Not only are these minerals of the greatest complexity as regards both the number and the nature of the elements of which they are made up, but also the separate estimation of tantalum, columbium, and titanium in presence of each other is up to now more or less approximate, and their separation from many other elements is beset with uncertainties. It is due chiefly to the difficulties encountered in their analysis that the true chemical affinities of the minerals in question are not yet quite clearly understood.

The present research, which it is intended shall be as comprehensive as possible, aims at improving the state of our knowledge of these minerals by testing the accuracy of published analytical methods and, if possible, by improving them and devising new ones. For some time past the authors have been studying the literature on the subject and investigating methods in the laboratory. The conclusions drawn by other workers in this field are frequently contradictory, and a repetition of some of the earlier work is needed in order to clear up debatable points. As the authors' time available for this investigation is limited, they have enrolled the help of collaborators, who will report on the result of their labours in due course. The whole research will form a connected series of papers appearing under the above general title.

I. *The Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates.*

This section is in the nature of a preliminary communication, being devoted to certain considerations on the analysis of tantalocolumbates and the brief description of a method of analysis which we have worked out and intend to elaborate more fully; so far it has given promising results with tantalite and columbite.

The best known and most generally applied method for the analysis of minerals of this group is what will hereafter be termed the pyrosulphate-hydrolysis method, that is, decomposition of the mineral by fusion with alkali pyrosulphate followed by prolonged boiling of the solution of the melt in order to precipitate the earth acids. This procedure is by no means above criticism, but as far as the decomposition of the mineral is concerned we feel strongly inclined to favour pyrosulphate as having a wider range of usefulness than potassium hydroxide or carbonate, potassium hydrogen fluoride, or hydrofluoric acid. As regards the hydrolysis of the solution resulting from the pyrosulphate melt, this process has several disadvantages; thus, the earth acids are not precipitated completely if the acidity of the solution is too great; the complete precipitation of the earth acids is not easily ascertained; and the precipitate—whether the acids are completely precipitated or not—is always contaminated with other elements, some of which are wholly, others partly, precipitated (silica, titania, tungsten, tin, antimony, iron, zirconia). It is opportune here to recall that the elements in presence of each other may lose their individuality: “the reactions these elements undergo when they occur alone do not necessarily occur when the two elements are mixed together (Mellor, “Quantitative Inorganic Analysis,” 1913, p. 496). F

example, columbium by itself is most difficult to precipitate completely by hydrolysis, but the presence of even a small quantity of tantalum causes complete precipitation (Meyer and Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," p. 183). Titanium has the reverse effect on columbium, as it impedes the precipitation (Mellor, *op. cit.*, p. 420), whilst the hydrolysis of titanium is adversely affected by zirconium (Hillebrand, *Bull. Geol. Survey, U.S.A.*, No. 422, p. 136). Therefore, if only the four elements named are present in the solution, the process of hydrolysis is a sufficiently complex reaction, which is at present being investigated.

The impure precipitate produced by hydrolysis must next be resolved into its constituents, and this again is a troublesome procedure. The first step consists in dissolving the earth acids in a suitable solvent, filtering off any residue, and again hydrolysing the filtrate. Three solvents are mentioned in the literature: (1) Basic ammonium tartrate, by Hoffmann and Prandtl (*Ber.*, 1901, 34, 1064): they merely state that the precipitate obtained after the hydrolysis was extracted with the compound mentioned. (2) Mannitol (Hauser, *Zeitsch. anorg. Chem.*, 1908, 60, 231; Hauser and Herzfeld, *Centr. Min.*, 1910, 758): the precipitate is treated with a 20 per cent. potassium hydroxide solution containing 10 per cent. of mannitol, the insoluble gangue filtered off, and the filtrate freed from lead and iron by ammonium sulphide. The filtrate is boiled under reflux, any zirconium remaining in solution; the reprecipitated earth acids are still accompanied by titanium, tin, antimony, and silica. (3) Hydrogen peroxide (Weiss and Landecker, *Zeitsch. anorg. Chem.*, 1909, 64, 65): the precipitate obtained by the hydrolysis is digested with 10 per cent. sulphuric acid and an equal volume of 3 per cent. hydrogen peroxide; the residue consists of gangue, silica, and lead sulphate. The filtrate is again submitted to hydrolysis with sulphurous acid, which precipitates tantalum, columbium, titanium, tungsten, tin, and antimony; iron and zirconium remain dissolved.

Regarding the last-named process, it must here be mentioned that divergent views have been expressed on the solubility of tantalalic acid in hydrogen peroxide. Noyes (*Chem. News*, 1906, 93, 180) and that it remained in large part undissolved, but Giles (*ibid.*, 1907, 95, 1) showed that it dissolved completely "when diffused dilute hydrochloric or sulphuric acid on addition of sufficient pure hydrogen peroxide (Merek's 'perhydrol')." In a recent communication, however, Hahn and Gille (*Zeitsch. anorg. Chem.*, 1920, 2, 283) report that tantalalic acid precipitated from hot solutions is almost insoluble, and when precipitated in the cold is very slightly soluble, in acid hydrogen peroxide; and that it reduces the

solubility of columbic and titanic acids. They draw the conclusion that Weiss and Landecker's method is inapplicable in presence of tantalie acid. In view of these conflicting statements, it would seem that the matter must be once more investigated.

The second step in the purification of the precipitate obtained by the hydrolysis consists in removing tungsten, tin, and antimony by digestion with ammonium sulphide (Berzelius) or by fusion with sodium carbonate and sulphur (Rose). These methods have however been condemned by Giles (*Chem. News*, 1909, **99**, 11, Smith (*Proc. Amer. Phil. Soc.*, 1905, **44**, 40), and Blomstrand (*J. pr. Chem.*, 1919, [ii], **99**, 40). Giles separates tin and antimony from the earth acids by fusion with potassium carbonate, solution of the melt in citric acid, and precipitation of tin and antimony by hydrogen sulphide; we propose the somewhat similar process described below. The methods for the separation of tungsten will shortly be submitted to a critical study.

Authors' Proposed Method.—The above considerations induced us to seek improvements in the analysis of tantalum-columbium minerals by evolving a different process while retaining pyrosulphate as a flux. The guiding idea was to avoid an initial hydrolysis for the precipitation of the earth acids and to attempt a preliminary purification of the solution by the removal of as many metals as possible, followed by a modified or improved process of hydrolysis. Now it is well known that tartaric acid prevents the precipitation of the hydroxides of tantalum, columbium, titanium, etc., and we ascertained that a concentrated solution of tartaric acid dissolves the cake from the pyrosulphate fusion of the minerals in question to a perfectly clear solution (compare Powell, *J. Soc. Chem. Ind.* 1918, **37**, 285r). We fuse 1 gram of the finely powdered mineral with 6 grams of sodium pyrosulphate in a silica crucible, adding sulphuric acid and again fusing if the melt solidifies before the decomposition is complete, and leach the cold mass with a solution of 10 grams of tartaric acid in not more than 50 c.c. of water. The insoluble residue contains any quartz, cassiterite, gangue, lead sulphate, and possibly some unattacked mineral; if this should be the case, fusion with pyrosulphate and extraction with tartaric acid are repeated on the ignited residue, when all the decomposable material is obtained in solution. The residue is analysed for lead, tin, silica, etc., whilst the combined filtrates are saturated with hydrogen sulphide; in this manner antimony, copper, traces of tin, and any other metals of the hydrogen sulphide group are eliminated and estimated. The filtrate, on digestion with ammonia and ammonium sulphide, yields a precipitate containing all the iron and uranium, as well as a small part of the manganese, if this meta-

be present. Manganese, as is known, is but imperfectly precipitated as sulphide from tartrate solutions (compare Mellor, *op. cit.*, p. 363).

The operations so far described eliminate certain rather troublesome elements (for example, silica, iron, tin, antimony), whilst tantalum and columbium are in solution, still accompanied by a number of their mineral associates. The following may be present: tungsten, titanium, and zirconium; rare-earth metals and thorium; aluminium, glucinum, manganese, calcium, and magnesium. We are now striving to find an accurate and comparatively simple method to resolve this complex mixture into its components.

We have already investigated, but without success, a scheme for separating titanium and zirconium as phosphates from tantalum and columbium in tartaric acid solution. We ascertained that ammonium phosphate does not precipitate the earth acids from tartrate solutions containing free tartaric acid, even on boiling, whilst zirconia is not precipitated in the cold, but boiling causes quantitative precipitation. It seemed therefore possible to separate zirconium from tantalum and columbium by leaching a pyrosulphate melt of the mixed oxides with sodium hydrogen tartrate and adding ammonium phosphate to the boiling solution. Under these conditions, however, when zirconia by itself would have been precipitated as phosphate, no precipitate was obtained in presence of tantalum and columbium, which provides another example of "loss of individuality." It was only when a fair excess of sulphuric acid was added to the solution that precipitation ensued, but the results calculated to zirconia were too high, due to contamination with several units per cent. of earth acids. As regards titania, this was only slowly and incompletely precipitated by ammonium phosphate from tartrate solutions acidified with sulphuric acid.

Summary.

The usual procedure for the analysis of tantalum-columbium minerals is briefly discussed. A new method of analysis is outlined, in which the initial hydrolysis is avoided by solution of the pyrosulphate melt in tartaric acid solution.

II. The Separation of Zirconium from Tantalum and from Columbium.

The pyrosulphate-hydrolysis method, outlined in section I of this paper, is so far the only one available for separating zirconium from tantalum and columbium, Bailey's hydrogen peroxide method

(T., 1886, 49, 149, 481) having proved untrustworthy (Meyer and Hauser, *op. cit.*).

A process of separation, based on an entirely different principle, was indicated by Hauser and Herzfeld in a paper on an occurrence of blomstrandine in the Urals (*Centr. Min.*, 1910, 758). They give a very brief outline of the procedure used in analysing the mineral, and state that they intended shortly afterwards to publish a detailed description of the most up-to-date procedure for the analysis of minerals of the earth acids—an intention which does not appear to have been carried out. The published method includes the following particulars for the separation of zirconia from the earth acids. The mixed oxides are fused with potassium hydroxide in a silver dish, the melt being continually stirred with a silver spatula; the melt is extracted with water and the residue filtered off; this is ignited and again fused as before. The insoluble residue from the second fusion is to be regarded as zirconia ("*ist als Zirkonerde anzusehen*") which must, however, still be tested for the presence of titania. The proportions of the constituents in question are reported thus: $\text{Cb}_2\text{O}_5 = 15.08$; $\text{Ta}_2\text{O}_5 = 1.30$; $\text{ZrO}_2 = 0.50$ per cent.

The wording of the above quotation referring to the purity of the residual zirconia is rather guarded, and as far as we know, no critical study of the potassium hydroxide fusion has yet been published. Giles pointed out (*Chem. News*, 1909, 99, 1) that zirconia was unaffected by fusion with potassium carbonate, and expressed the opinion that this might answer as a means of separating zirconia from tantalum and columbium. He did not carry out any test separations to prove that the method was quantitative. We therefore decided to investigate it by working with the pure oxides. Those of tantalum and columbium were prepared from the carefully recrystallised double fluorides, whilst the zirconia was obtained from recrystallised zirconyl chloride prepared from zircon.

For reasons explained below we confined ourselves almost entirely to the use of potassium carbonate. In a preliminary experiment, 0.25 gram of each oxide was fused by itself with 2.5 grams of potassium carbonate in a platinum crucible; the melt was leached with hot water, the solution filtered off, acidified with hydrochloric acid, and boiled with a slight excess of ammonia and filter-pulp; the precipitate was ignited and weighed. The filter containing the residue from the fusion was washed with dilute hydrochloric acid to remove any potassium salt, the liquid boiled, made ammoniacal, and again filtered through the same paper, which was ignited and the residue weighed; in the case of tantalum and columbium pentoxides this residue was again fused with 2 grams of potassium

carbonate, giving a second soluble fraction and a final residue. It is interesting to note the ease with which columbium pentoxide is attacked by potassium carbonate at the melting point of the salt, whilst the reaction between tantalum pentoxide and potassium carbonate requires the heat of a very powerful blast burner. The weight of the final products was in excess of that originally taken owing to unavoidable contamination: we were unable to obtain chemically pure potassium carbonate, and the best article procurable was not quite free from silica and iron. In addition, the crucible was more or less strongly corroded by the fused alkali, which led to further contamination by platinum. The results of the preliminary tests are tabulated below.

Weight of substance taken. Gram.		Weight of products.			Remarks.
		From first fusion.	From second fusion.	Total products.	
0.2512 ZrO_2	Insoluble	0.2562	—	0.2562	
	Soluble	0.0013	—	0.0013	black (Pt).
0.2503 Ta_2O_5	Insoluble	0.0242	0.0074	0.0074	black.
	Soluble	0.2285	0.0182	0.2467	
0.2500 Cb_2O_5	Insoluble	0.0090	0.0012	0.0012	brown.
	Soluble	0.2434	0.0068	0.2502	

The following procedure was used in the test separations. The pure weighed oxides were fused with potassium pyrosulphate in a silica crucible until a clear melt was obtained; this was leached with water and the turbid liquid boiled with filter-pulp and a slight excess of ammonia. The precipitate was filtered off, washed with dilute ammonium nitrate solution, and strongly ignited in a platinum crucible. This preliminary treatment resulted in the production of an intimate mixture of finely divided oxides such as would be obtained in an analysis. The mixed oxides were fused with potassium carbonate (5 to 20 parts) over a powerful blast burner until the fusion was tranquil. The cold melt was leached with hot water in platinum or porcelain and the liquid filtered through close-textured paper. It was, as a rule, necessary to re-filter once or even twice through the same paper, as the finely-divided zirconia gave a turbid filtrate at the start. The insoluble residue was washed with 2 per cent. potassium carbonate solution. The filtrate was acidified with hydrochloric acid and boiled with filter-pulp and a slight excess of ammonia; the precipitate was filtered off, washed with water containing ammonium nitrate, strongly ignited in a platinum crucible, and weighed. The residue from the leaching of the melt was washed with dilute hydrochloric acid, the washings were boiled with a slight excess of ammonia, again filtered through the same paper, the latter was ignited with

the residue and weighed; the weighed residue was again fused with potassium carbonate, etc., giving a second soluble fraction and residue. The latter was fused a third time, yielding a third soluble fraction and a final residue (zirconia). The precipitates from the three soluble fractions (tantallic acid) were combined. In the separation of zirconia from columbium pentoxide only two fusions were made.

The final products were purified in the following manner. The zirconia residue was fused with pyrosulphate and the melt leached with cold dilute sulphuric acid to prevent the precipitation of the small quantity of tantallic acid present. The solution was precipitated with hydrogen sulphide after addition of a little filter-pulp for the purpose of collecting the platinum sulphide; the precipitate was filtered off, well washed, ignited, and weighed; it was then fused with a little pyrosulphate, the melt leached with concentrated tartaric acid solution, and the residue filtered off, ignited, and again weighed to ascertain its freedom from tantallic acid; the difference between the first and second weight, if any, was added to the weight of the zirconia. The filtrate from the platinum sulphide was nearly neutralised with sodium carbonate, and boiled for an hour with sodium thiosulphate. The precipitate was filtered off, washed, ignited, leached with dilute acid, the liquid made slightly ammoniacal, filtered again through the same paper, and the washed precipitate ignited and weighed as zirconia.

The combined tantallic (columbic) acid fractions were fused with pyrosulphate in a silica crucible; the melt was leached with concentrated tartaric acid solution, the residue filtered off, ignited, and again fused as before. The melt was again leached with tartaric acid solution, and the two combined leach liquors were treated with hydrogen sulphide and a little filter-pulp. The precipitate, containing platinum and any siliceous matter present, was filtered off, washed, ignited, and weighed. This weight was subtracted from that of the combined earth acid fractions, and the difference reckoned as tantalum (columbium) pentoxide. The table on page 1935 shows the results obtained.

The figures prove that the amount of tantallic acid rendered soluble in the first fusion was independent of the proportion of potassium carbonate used: in expts. 14—17 this amounted to 2.5 grams; in expt. 18, to 5 grams; and in expt. 20, to 10 grams.

In expt. 19, the mixed oxides were fused with 3.5 grams of potassium hydroxide in a nickel crucible, at first gently for half an hour, then strongly for twenty minutes. The result shows that potassium hydroxide is less effective than the carbonate, which is to be ascribed to the lower temperature at which the fusion is

necessarily conducted; at a red heat, the fused alkali creeps over the edge of the crucible, and contamination of the melt with nickel becomes pronounced. The use of potassium hydroxide was therefore abandoned.

Expt.	Weight of substance taken.		Weight of products.				Purified oxides.	Error.	Grams of K_2CO_3 used in each fusion.
			From first fusion.	From second fusion.	From third fusion.	Total products.			
14	0.2504 ZrO_2	Insoluble	0.2830	0.2594	0.2554	0.2354	Not purified.		(1) 2.0
	0.2501 Ta_2O_5	Soluble	0.2134	0.0324	0.0066	0.2521			(2) 2 (3) 2
15	0.2510 ZrO_2	Insoluble	0.3496	0.2644	0.2562	0.2362	0.2539	+0.0020	(1) 2.5
	0.2504 Ta_2O_5	Soluble	0.1658	0.0764	0.0090	0.2512	0.2382	-0.0022	(2) 2 (3) 2
16	0.2503 ZrO_2	Insoluble	0.2700	0.2686	0.2614	0.2614	0.2583	+0.0080	(1) 2.5
	0.2495 Ta_2O_5	Soluble	0.2318	0.0055	0.0122	0.2475	0.2414	-0.0081	(2) 2.5 (3) 2.5
17	0.0126 ZrO_2	Insoluble	0.0486	0.0272	0.0214	0.0214	0.0186	+0.0060	(1) 2.5
	0.2502 Ta_2O_5	Soluble	0.2186	0.0205	0.0120	0.2511	0.2461	-0.0041	(2) 1 (3) 2.5
18	0.2534 ZrO_2	Insoluble	0.3028	0.2736	0.2682	0.2682	0.2568	+0.0054	(1) 5
	0.2509 Ta_2O_5	Soluble	0.2174	0.0342	0.0086	0.2602	0.2476	-0.0033	(2) 3 (3) 3
19	0.2511 ZrO_2	Insoluble	0.3475	0.2970	—	—	—	—	(1) 2.5
	0.2520 Ta_2O_5	Soluble	0.1657	—	—	—	—	—	(2) 3 (3) 3
20	0.2521 ZrO_2	Insoluble	0.3083	—	—	—	—	—	(1) 10
	0.2530 Ta_2O_5	Soluble	0.2260	—	—	—	—	—	—
21	0.2509 ZrO_2	Insoluble	0.2661	0.2563	—	0.2563	0.2515	+0.0006	(1) 5
	0.2520 Cb_2O_5	Soluble	0.2673	0.0045	—	0.2718	0.2511	-0.0009	(2) 3
22	0.2504 ZrO_2	Insoluble	0.2551	—	—	0.2551	0.2513	+0.0008	(1) 5
	0.2502 Cb_2O_5	Soluble	0.2514	—	—	0.2514	0.2498	-0.0004	—

Conclusions.

The separation of zirconia from columbium pentoxide by fusion with potassium carbonate is quantitative within the limits of experimental error. It is advisable to submit the fusion residue to a second fusion.

The separation of zirconia from tantalum pentoxide by fusion with potassium carbonate is less satisfactory than the preceding. Even after three fusions, the results show a positive error of 2—8 mg. for zirconia, and a corresponding negative error for tantalum pentoxide. Roughly speaking, 80 to 90 per cent. of the tantalic acid present is rendered soluble in the first fusion.

The fusion method described in this section should prove more especially useful for estimating zirconia in columbate minerals poor in tantalum. It may also be applied in the analysis of tantalocolumbates for checking the purity of zirconia precipitates, or ascertaining the presence of small quantities of zirconia in precipitates obtained by the usual method of hydrolysis.

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CCXXI.—*Catalysis of the Mutarotation of Dextrose by Metals.*

By WILLIAM EDWARD GARNER and DOUGLAS NORMAN JACKMAN.

IN the course of experiments on the action of an electromagnetic field on the mutarotation of dextrose, it was observed that a field of approximately 20,000 gauss affected neither the rate of change of the reaction nor the concentration of the equilibrium mixture. A marked acceleration of the mutarotation was, however, noticed on repeating the experiments with nickel in the polarimeter tube. This phenomenon was subsequently shown to be due to the direct catalytic activity of metallic nickel, and not to any superimposed electromagnetic effect. Very little work appears to have been done on the effect of metal surfaces on the mutarotation of sugars, and no reference has been found in the literature to the catalytic effect of metals like nickel. The platinum metals have, however, been shown by Plzak and Husek (*Zeitsch. physikal. Chem.*, 1904, **47**, 733) to catalyse the rate of inversion of sucrose.

The mutarotation of dextrose is markedly accelerated by catalysts producing hydroxyl ions, and to a less extent by hydrogen ions, and it was possible that the function of the metal was to supply one of these ions. On the other hand, the catalysis of hydrogenation processes by metallic nickel made it possible that the acceleration was caused by some surface action. The observation was thus of interest, and an investigation promised to throw light on catalysis by metallic nickel in hydrogenation processes.

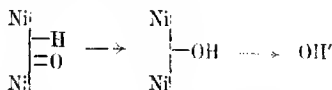
The greater part of the work described in the present communication has been carried out with metallic nickel, but preliminary experiments have shown that the nickel may be replaced by cobalt, iron, and copper. The dextrose could also be replaced by other sugars. The activity of the metals was considerably increased by a preliminary oxidation and reduction of the surface, and the temperature at which the reduction was carried out had an important bearing on the activity of the metal. The best temperature for the reduction of the nickel was 340–440°; when reduced above or below these temperatures, the metal shows a much smaller activity.

The action of the catalyst was not uniform from the beginning to the end of the reaction; there was an induction period in the beginning, and a decline in the activity of the catalyst towards the end. This decline in the activity of the catalyst is a phenomenon which is frequently observed in hydrogenation with metallic nickel (Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, **54**, [B], 113).

The decrease in the activity of the surface was accompanied by the dissolution of some of the metal. This dissolved or dispersed metal is still active in solution, as was demonstrated by adding it to a freshly prepared dextrose solution. The activity of the solution, however, declines slowly; a change which is probably associated with the formation of a compound of the metal with dextrose.

The surfaces of cobalt and nickel are attacked by water, with the formation of hydroxide and the liberation of hydroxyl ions. The surface of the reduced metal is attacked more rapidly than that of either the untreated or oxidised metal. The rapidity of production of hydroxyl ions by the metal runs roughly parallel with its effect as a catalyst on the mutarotation of dextrose. Thus cobalt, which gives rise more readily to hydroxyl ions than metallic nickel, is also the more effective as a catalyst.

It is difficult to state definitely the source of this hydroxyl ion. Since the catalysis is not decreased by the replacement of the oxygen in the water by hydrogen, it is evident that dissolved oxygen plays but a small part. There appear to be two alternative sources, (a) a sub-oxide of the metal, and (b) adsorbed hydrogen and oxygen on the surface. In the former case hydroxyl ions would be formed by the interaction of the oxide with water, and in the latter case the adsorbed gases could unite in the presence of water to give this ion. Thus:



The catalytic activity of the metals in the platinum group is generally ascribed to the presence of hydrogen and oxygen. Mond, Ramsay, and Shields (*Phil. Trans.*, 1898, [A], **191**, 105) showed that both hydrogen and oxygen can exist together in metallic palladium. Willstätter (*loc. cit.*) emphasises this point and puts forward a theory of catalysis in which the catalyst is a compound of platinum with both hydrogen and oxygen. Brochet expressed an opinion that pure nickel is catalytically inactive, and this has recently been confirmed by Willstätter, who finds that the most readily reduced organic compounds cannot be hydrogenated in the presence of nickel which has been completely freed from oxygen. This inactive nickel can, however, be activated by priming with oxygen.

It thus appears that the source of the hydroxyl ions is either the sub-oxide or the hydrogen and oxygen adsorbed on the nickel or cobalt surface. This is in accordance with the experiments

with oxidised metals; the activity of an oxidised metallic surface is always much smaller than that of a reduced surface. An explanation is also provided for the relative inactivity of metallic nickel, when reduced at high temperatures, for in this case the dissolved or combined oxygen is probably almost completely removed.

The catalysis by nickel is almost entirely inhibited by the addition of small amounts of hydrochloric acid, the effect not being permanent if the acid is neutralised within a few minutes. Much greater concentrations of acid are required to render the surface of cobalt passive, for in this case the tendency for the formation of hydroxyl ions is much greater.

Alkali, either sodium or ammonium hydroxide, although speeding up the mutarotation, is without effect on the catalyst, the catalytic reaction proceeding at almost the same rate in alkaline as in pure aqueous solution.

The temperature coefficient of the catalytic reaction is doubled every five degrees, being almost the same as the temperature coefficient of the normal reaction. It is thus unlikely that the reaction occurs on the surface of the solid metal; for the temperature coefficient of such heterogeneous catalytic reactions rarely exceeds 1.3 per 10°. The acceleration of the mutarotation must therefore be due to a catalyst, present in the solution.

The published experimental data on the catalysis of the mutarotation of dextrose by hydroxyl ion are very conflicting. The concentrations of the hydroxyl ion are usually determined from hydrolysis and dissociation constants and the calculations are frequently subject to considerable errors. Asaka (*Zeitsch. physikal. Chem.*, 1900, **35**, 685) finds values for $\frac{K}{c_{OH}} \times 10^{-4}$, varying with the source of the hydroxyl ion; K is the velocity constant and c_{OH} the concentration of the hydroxyl ion. Some of the results are given below and it will be seen that the amounts of hydroxyl ion required to double the velocity constant in neutral solution vary between 1.0×10^{-4} and $1.0 \times 10^{-6} N$.

Source of OH'.	Temp.	$\frac{K}{c_{OH}} \times 10^{-4}$.	[OH'] required to double K .	Author.
NH ₄ OH } NH ₄ Cl }	25°	1.5	1.3×10^{-6}	Osaka.
Pyridine	"	0.22	9.0×10^{-6}	"
Aniline	"	0.19	10.0×10^{-6}	"
Na ₂ CO ₃	20	0.0133	1.1×10^{-4}	Murschauser.*

* *Biochem. Zeitsch.*, 1920, **108**, 23.

The question now arises as to whether sufficient hydroxyl ion

is produced by the metallic surface to account for the catalysis that is obtained. From Tables V and VI it will be observed that $N/50,000$ to $N/100,000$ acid is sufficient to inhibit the catalysis with metallic nickel, therefore the total amount of hydroxyl ion produced in the dextrose solution cannot be greater than corresponds with these concentrations of acids. These values are intermediate between the concentrations of Osaka and Murschauser, which were required to double the rate of mutarotation. We are thus unable to state definitely that the hydroxyl ion is the sole cause of the catalysis, but since the concentrations of hydroxyl ion produced in the polarimeter tube are of the same order as those found to be effective by Osaka, it would seem that this explanation of the catalysis is the most satisfactory that can be put forward.

EXPERIMENTAL.

Purity of Dextrose.—The catalytic activity of nickel is dependent on the purity of the dextrose and particularly on its acidity. Acid behaves as a negative catalyst even when the concentration present is insufficient to increase appreciably the rate of mutarotation. The greatest acceleration of the rate of mutarotation was given by a quantity of Kahlbaum's dextrose which was neutral to litmus. Dextrose, free from acid and crystallised many times from alcohol and water, usually gave a lower activity than this dextrose. Dextrose from several sources, purified in different ways, could always be catalysed to some extent by metallic nickel.

Purity of Nickel and Cobalt.—Nickel was used as foil and in the form of spheres. The former was a pure sheet nickel and the latter the pure metal supplied by the Mond Nickel Co. The surface of the metal was found to deteriorate with continued use, but its activity could be restored by cleaning with emery cloth. Different batches of the nickel spheres varied greatly in their behaviour on oxidation and reduction and in their activity. In some cases expansion of the nickel spheres occurred on oxidation and cracks frequently developed. These irregularities made the reproducibility of results somewhat difficult.

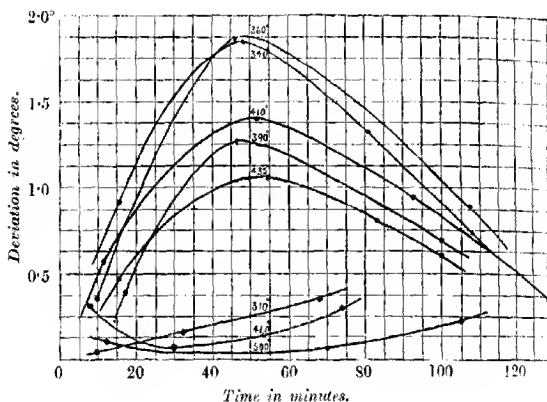
The magnitude of the effect with untreated metallic nickel was dependent on the manner of cleansing of the nickel surface; thus, when cleaned with alcohol and ether, the surface was more active than when cleaned with hydrochloric acid.

The cobalt contained traces of iron, but was free from nickel.

Apparatus.—The catalysis was carried out in polarimeter tubes, which were gently rocked on a platform between the polariser and the analyser by means of a crank and motor, and a constant rate of

stirring was secured by means of a small opaque glass bead, which traversed the whole length of the tube. A constant temperature was maintained by circulating a stream of water at 25° through the outer jackets of the polarimeter tubes arranged in parallel. The activity of the nickel surface was found to be increased by a preliminary oxidation and reduction. It was necessary to standardise carefully the conditions under which the oxidation and reduction were carried out. Gas furnaces were first employed for both the oxidation and reduction, but in the majority of the experiments the reduction was effected in an electric furnace. The active material was employed in several forms. Thus in some cases tubes of foil closely fitting the internal surface of the polarimeter tube were

FIG. 1.



employed as catalysts. Nickel spheres of about 0.4 cm. diameter and strips of metal were also used.

The readings were taken as rapidly as possible, by stopping the rocker and holding the tubes in position. The average time taken to read each tube was one minute.

Temperature of Reduction and the Activity of the Nickel.

Nickel spheres were oxidised in a nickel tube at approximately 800° for half an hour and then placed in a platinum boat and reduced at a constant rate of flow for one hour and cooled to 100° in electrolytic hydrogen. The electric furnace was suspended, so that it could be gently rocked during the operation.

The appearance of the nickel spheres after this treatment varied with the temperature of reduction; below 300° the surface was a dull grey, and above 340° it had a bright metallic appearance. The dull grey surface was rarely active. Kahlbaum's dextrose was employed throughout, and the concentration of the solution was 10 per cent. by weight of dextrose. This concentration was employed throughout the work. Twenty spheres of a total area of 3.2 sq. cm. were used in each 2-dm. tube. The results are summarised in Table I and Fig. 1. The differences between the polarimeter readings of the blank and of the tube containing the nickel spheres are plotted against the time in minutes. The maximum difference between the two readings usually occurred at about forty-eight minutes if the spheres were appreciably active. The maximum deviations for each temperature of reduction are given in the table, and the appearance of the spheres is noted.

TABLE I.

Temp.	Maximum deviation.	Appearance.	Temp.	Maximum deviation.	Appearance.
500°	0.04°	Bright.	360°	1.88° *	Bright.
460	0.14	„	340	1.84° *	„
435	1.10	„	310	0.26	Dull.
410	1.42	„	290	unchanged	Black.
390	1.26	„			

* Effects of this magnitude were only produced with Kahlbaum's dextrose.

The maximum activity under these conditions is obtained by reduction at 340—360°.

Temperature Coefficient of Catalytic Reaction.

The catalytic action of nickel on dextrose solution was compared at two temperatures, 7° and 26°, and of cobalt at 3.8° and 26°. The two metal strips of equal surface area employed in each experiment were cut from the same sheet, and oxidised at the same temperature and reduced at 380°, side by side in the furnaces. The activity of the two strips was as nearly as possible the same. The temperature of the polarimeter tubes was maintained at the above values by streams of water through the outer jackets. The maximum deviation between the polarimeter readings of the blank experiment and the tube containing the metal was greatest for the lower of the two temperatures; thus a deviation of 1.46° at 7° against 0.87° at 26° occurred with the metallic nickel. These deviations are not a measure of the relative speeds of the reaction, as will be seen from the velocity constants over the first three-

quarters of the reaction, given in Table II. The velocity constants are calculated from the formula, $K = \frac{1}{t} \log \frac{a}{a-x}$.

TABLE II.

Metal.	Temp.	Maximum deviation.	K Blank.	K Metal.	$\frac{K \text{ Metal}}{K \text{ Blank}}$
Nickel	7°	1.46°	0.00160	0.00226	1.41
"	26°	0.87	0.0119	0.0173	1.45
Cobalt	3-8°	4.15	0.00134	0.00369	2.76
"	26°	2.55	0.0124	0.0340	2.74

The ratio of $\frac{K \text{ metal}}{K \text{ blank}}$ is the same at the two temperatures, showing that in the cases of both nickel and cobalt the temperature coefficient of the catalytic reaction is almost identical with that of the normal reaction. The velocity constant is thus doubled for every 5° rise in temperature.

Deterioration of the Activity of the Surface.

The deterioration of the surface with time is mainly caused by the dissolution of the active metal. The nature of the effect can be seen from the following typical results.

The metal after use in one experiment was immediately washed with dextrose solution, transferred to a newly-made solution, and the rate of mutarotation determined. When nickel spheres were used, the activity of the metal was completely destroyed after use in one experiment, but with the more active nickel and cobalt strips, the metal still possessed residual activity. The following mean velocity constants for the first hour of the mutarotation illustrate this effect.

TABLE III.

No.	Temp.	Metal.	K.	K.
1.	25°	Nickel freshly reduced.	0.0144	used again. 0.0122
2.	25	Blank.	0.0114	0.0113
3.	27	Cobalt freshly reduced.	0.0245	used again. 0.0177
4.	27	Blank.	0.0122	0.0122

Since it was possible that the activity of the metal had been transferred to the solution, the liquid from a previous experiment was mixed with a freshly prepared solution of dextrose. When the spheres were used, the solution was frequently inactive, but occasionally the liquid itself contained active material, which was

able to catalyse the speed of reaction of a fresh solution. Thus in the two experiments above, when 50 per cent. of the solution from (1) or (3) was added to a fresh dextrose solution, the rates of mutarotation were greater than when 50 per cent. of either of the solutions (2) and (4) was added to a fresh dextrose solution. From (1) $K = 0.0129$, (2) $K = 0.0113$, (3) $K = 0.0153$ and (4) $K = 0.0122$.

Kahlbaum's dextrose recovered by evaporation of the aqueous solution to dryness, gave the normal velocity of mutarotation, although it contained nickel.

The metal goes into solution as hydroxide, for both hydroxyl ions and the metal cations can be detected in the solutions. A freshly reduced cobalt surface is rapidly attacked by distilled water, liberating hydroxyl ions. The effect with untreated or oxidised cobalt is much smaller. The concentration of hydroxyl ions in the experiments with cobalt and dextrose was about $N/20,000$ at the end of the mutarotation, and this concentration is sufficiently great to account for the observed catalytic effect (Hudson, *J. Amer. Chem. Soc.*, 1907, 29, 1574).

Nickel slowly gives hydroxyl ions with water, but no hydroxyl ions could be detected in the dextrose solutions by means of litmus, even in the middle of the experiments. Since the alkalinity of the dextrose solutions slowly decreases on keeping, it is probable, that, in the case of nickel, hydroxyl ion is only present in the neighbourhood of the nickel surface.

The Effect of Dissolved Oxygen.

Since water containing oxygen attacks cobalt and nickel, it was possible that the oxygen dissolved from the air was responsible for the catalysis. Water was freed from oxygen and carbon dioxide by boiling, and saturated with hydrogen. When the water had cooled to the ordinary temperature, dextrose was introduced without admitting any air to the apparatus. The solution of dextrose was rapidly transferred to a polarimeter tube containing either reduced nickel or cobalt. At the same time, a dextrose solution was made up in distilled water saturated with air, and the effect of a strip of metal determined. The two strips were cut from the same sheet and were reduced side by side.

The catalysis was somewhat greater in the boiled solution than in the solution containing air, possibly owing to the removal of carbonic acid, which when present would reduce the hydroxyl-ion concentration. It is thus clear that the catalysis is not determined by the oxygen dissolved in the water.

Acidity and Alkalinity of the Dextrose Solution.

The addition of small quantities of sodium hydroxide or hydrochloric acid to the dextrose solutions yielded interesting results. The experiments are divided into two series, the first a preliminary series with nickel tubes and the second with nickel spheres, carried out after more experience had been gained. In the preliminary series sometimes new tubes and at other times the old tubes newly reduced were used. This was unsatisfactory, as the activity of the tubes changed with use. It was thus necessary to take the mean of the results. Acid was found to destroy the activity of the nickel, whereas alkali on the whole did not appear to decrease the catalytic effect. Since carbon dioxide was not removed from the solution, the alkali may have been present as carbonate, but at these dilutions the degree of hydrolysis is considerable. The maximum lead in degrees given by the nickel tube over the blank is given in Table IV. From the mean values the effect of the alkali is seen to be slight. The effect of continued use with alkaline dextrose solutions is seen in the last row of figures.

Ammonia appears to resemble sodium hydroxide in its action.

TABLE IV.

Effect of Alkali on the Catalysis.

Normality of NaOH.	Maximum lead.	Mean ₄
None	1.4, 0.62, 0.95, 0.80	0.94
N/20,000	0.84	0.84
N/10,000	0.62, 0.76, 1.36, 0.75, 0.73	0.84
N/5000	0.87, 0.57, 1.01, 0.65	0.77
N/2500	1.03, 1.07, 0.86, 0.86	0.95
None *	0.50, 0.53, 0.28, 0.16	0.37

* Previously used with alkali.

It became evident that a nickel surface could only be used once if reproducibility of results was to be obtained. In the second series, it was therefore decided to use nickel spheres, since these could be replaced after every experiment and a large number could be oxidised and reduced at one time, under identical conditions. These spheres made possible comparative measurements with the same active surface of nickel, and experiments with acid and alkali could be carried out simultaneously. Four to six tubes were employed in each series of experiments, and a typical series contained the following experiments: (1) blank; (2) dextrose solution and twenty nickel spheres, 0.4 cm. in diameter; (3) dextrose solution and alkali; (4) dextrose solution, alkali, and nickel spheres; (5) dextrose solution and acid, and (6) dextrose solution, acid, and nickel spheres.

The magnitude of the catalytic effect varied with the different batches of spheres, and more difficulty was experienced in obtaining an active surface than with sheet nickel on account of the smaller area employed.

Concentrations of acid and alkali varying from $N/1000$ to $N/500,000$ were used. With alkali of greater concentration than $N/1000$, the speed of mutarotation was too great to be conveniently measured. The requisite quantity of acid or alkali was added as one drop of a solution of the necessary strength.

Results with Acid and Alkali.

The change in the velocity constants with time in some of the experiments is given in Table V. Where catalysis occurs, the velocity constants increase to a maximum value and then decrease.

TABLE V.

Acidity or alkalinity.	Velocity constant.	Mean <i>K</i> for the first hour.
Zero.	0.0104, 0.0093, 0.0097, 0.0101	0.0098
" + Ni.	0.0109, 0.0120, 0.0140, 0.0112	0.0123
<i>N</i> /1000-HCl.	0.0097, 0.0104, 0.0091, 0.0088	0.0098
" + Ni.	0.0093, 0.0100, 0.0034, 0.0084	0.0094
Zero.	0.0097, 0.0096, 0.0103	0.0097
" + Ni.	0.0142, 0.0148, 0.0067	0.0145
<i>N</i> /10,000-NaOH.	0.0110, 0.0109, 0.0095	0.0110
" + Ni.	0.0129, 0.0173, 0.0090	0.0150
<i>N</i> /10,000-HCl.	0.0111, 0.0102, 0.0094	0.0107
" + Ni.	0.0109, 0.0106, 0.0080	0.0108

The mean velocity constant for Kahlbaum's dextrose was 0.0098. In a series of experiments with dextrose supplied by the British Drug Houses, Ltd., the mean velocity constant was 0.0101; the rates of mutarotation, therefore, are very similar.

In Table VI the differences between the mean velocity constant of the blank and that with nickel are given, together with the maximum deviation.

TABLE VI.

Nature of dextrose.	Alkali and acid concentration.	Dextrose only.		Dextrose with alkali.		Dextrose with acid.	
		Vel. const.	Max. dev.	Vel. const.	Max. dev.	Vel. const.	Max. dev.
K.	$N/1000$	+ 0.0025	0.67°	—	—	— 0.0003	0.00°
K.	$N/10,000$	+ 0.0047	1.35	+ 0.040	0.72°	+ 0.0001	0.06
B.D.H.	"	+ 0.0060	0.90	—	—	+ 0.0002	0.15
B.D.H.	$N/50,000$	+ 0.0032	0.69	+ 0.054	0.71	+ 0.0017	0.22
* B.D.H.	"	+ 0.0037	0.78	—	—	+ 0.0002	0.06
B.D.H.	$N/100,000$	+ 0.0032	0.62	+ 0.028	0.50	+ 0.0003	0.25
B.D.H.	$N/500,000$	+ 0.0023	0.52	+ 0.010	0.23	+ 0.0006	0.15

* Nickel tubes.

The negative catalytic effect of hydrochloric acid is very marked up to a concentration of $N/50,000$; above this concentration up to $N/500,000$, the acid still reduces the activity of the nickel. On the other hand, alkali does not materially reduce the activity, except in the doubtful case of $N/500,000$ -alkali.

More nickel is detected in the solution when hydrochloric acid is present.

Cobalt was much less sensitive to hydrochloric acid, $N/10,000$, acid being insufficient to destroy the catalysis. A slight initial retardation is noticed, but after a few minutes the catalytic reaction proceeds at its full rate.

Effect of Metals and their Oxides on the Mutarotation of Dextrose.

In order to compare the effects of various metals, a number of metal strips were placed in the polarimeter tubes, and stirring was effected by means of an oxidised nickel sphere. The copper and iron were oxidised at 800° for ten minutes and the cobalt and nickel for half an hour; the strips were all reduced at 330° for half an hour. The values for the velocity constant at 25° are given in Table VII. The areas of the metal strips were only approximately the same, and the amount of active reduced metal differed greatly in the four cases. Owing to the difficulty of oxidising metallic nickel, the amount of reduced metal was much smaller than in the cases of iron and cobalt. Also the best temperature of reduction may not be the same for other metals as for nickel.

TABLE VII.

Various Metals.

Metal.	Area in sq. cm.	Velocity constant.					Percentage of metal in the solution.
		16 min.	39 min.	62 min.	78 min.	1st hr.	
Fe	40	0.0137	0.0164	0.0157	0.0125	0.0152	Not determined.
Ni	24	0.0118	0.0128	0.0125	0.0135	0.0123	0.0076
Cu	39	0.0118	0.0126	0.0119	0.0117	0.0121	0.022
Co	35	0.0234	0.0400	0.0490	—	0.0361	0.0035
Blank		0.0119	0.0112	0.0118	0.0115	0.0116	—

The amount of metal which goes into solution is no criterion of the activity of the metal.

The oxidised metal was always less active than the reduced metal, and in the case of nickel the oxidised material was practically inactive. Two series of experiments are given below, one in which nickel and cobalt and the other in which nickel and copper are compared with one another. In each series the five tubes were

compared simultaneously. The mean velocity constant for the first hour is given.

TABLE VIII.

Series.	Velocity constant.			
	Copper.	Nickel.	Cobalt.	Blank.
(1) Oxidised.	0.0113	0.0100	—	0.0100
(1) Reduced.	0.0174	0.0204	—	—
(2) Oxidised.	—	0.0100	0.0145	—
(2) Reduced.	—	0.0144	0.0297	—

Nickel in these and in other experiments always gave a higher acceleration of the mutarotation than copper. Oxidised cobalt catalyses the mutarotation of dextrose at about the same speed as reduced nickel.

The nickel solutions in series (2) were acid to phenolphthalein, and both cobalt solutions were alkaline to this indicator. The alkalinity of the solution in contact with the reduced metal was $N/6000$, whereas that in contact with the oxidised metal was $N/80,000$.

Other Sugars.

The property possessed by nickel of catalysing the rate of mutarotation was found to extend to other sugars than dextrose. Only qualitative experiments were made.

Lactose. Maximum deviation of 0.48° on 4.15° , 0.20° on 2.51° , and 0.22° on 2.37° .

Maltose. 0.25° on 2.91° .

Levulose. Slight effect.

Galactose. No effect.

Owing to the small quantities of maltose, levulose, and galactose available, no great importance can be attached to these results. It, however, appears from the lactose experiments that the catalytic action of nickel also takes place with other sugars.

Summary.

Nickel, cobalt, iron, and copper have been shown to catalyse the mutarotation of dextrose. The metals are more active after a preliminary oxidation and reduction of the surface, and the temperature of reduction has an important bearing on the activity of the metal. An oxidised metal surface is either inactive or gives a much smaller catalytic effect than the reduced surface.

The surface of the catalyst deteriorates with time, owing to the dissolution of some of the metal as hydroxide.

The hydroxyl-ion concentration obtained is of the same order as that necessary to produce the observed change in the velocity of mutarotation. The catalytic reaction is not caused by the oxygen dissolved in the dextrose solution, for the catalysis occurs in oxygen-free water, but is presumably associated with the oxygen and hydrogen dissolved by or in combination with the metal.

Very low concentrations of acid inhibit the activity of nickel and reduce that of cobalt, whereas alkali has but a slight effect on the catalytic reaction.

The velocity constant of the catalytic reaction is doubled for every 5°; it is thus unlikely that the catalysis occurs on the surface of the metal.

In conclusion, we wish to express our thanks to Professor F. G. Donnan for providing the facilities for this work.

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CCXXII.—*The Decomposition of Ozone by Light of the Visible Spectrum.*

By ROBERT OWEN GRIFFITH and WILLIAM JAMES SHUTT.

THE photochemical decomposition of ozone has been studied by Regener (*Ann. Physik*, 1906, [iv], 20, 1033), von Bahr (*ibid.*, 1910, [iv], 33, 598) and Weigert (*Zeitsch. physikal. Chem.*, 1912, 80, 78). All these investigators employed ultra-violet light, the effective deozoneising region being in the neighbourhood of 254 μ . It is also known that, in the presence of chlorine (compare Weigert, *Zeitsch. Elektrochem.*, 1908, 14, 591), light of longer wave-length, namely, that of the blue and violet portions of the spectrum, will cause ozone to decompose. The object of this investigation was to test, in a purely qualitative manner, whether ozone is decomposed by the action of light of still longer wave-length, that of 500 to 800 μ . In the general discussion on catalysis before the Faraday Society, September, 1921, W. C. McC. Lewis has shown, from theoretical considerations based on his radiation theory of chemical reactivity, that the longest wave-length of light capable of decomposing ozone in a unimolecular manner should be about 700 μ . This, however, does not eliminate the possibility that

shorter waves, in addition, may have the same effect. The results of this preliminary work seem to prove that ozone decomposes under the action of red and yellow light; but it is hoped, at a later date, to define the limits of the effective spectral regions with greater precision than is now possible.

EXPERIMENTAL.

The method adopted to ascertain whether photochemical decomposition of ozone occurs on illumination with light of the visible portion of the spectrum was that of following the pressure changes which take place when a constant volume of ozonised oxygen is subjected to light of constant intensity. Since two volumes of ozone are converted, when decomposed, into three volumes of oxygen, the extent of the decomposition may be calculated.

Ozone was prepared by the method of Fischer and Massenez (*Zeitsch. anorg. Chem.*, 1907, **52**, 202, 220), namely, the electrolysis of dilute sulphuric acid at a high anodic current density, using a water-cooled platinum anode. This was made by shaping a thin platinum tube of $3\frac{1}{2}$ mm. external diameter into the form of a U, the two vertical limbs being about 5 cm. in length, the horizontal portion 3 cm. The two ends were silver-soldered into two stout copper tubes. The horizontal portion of the anode was sealed into blue enamel glass, which was then carefully filed down at one side so as to expose a platinum surface of 6×0.5 sq. mm., and the remainder of the tube was given several coats of paraffin wax. The anode was placed in the central limb of a double H vessel, the two outer limbs of which contained lead cathodes, and the horizontal connecting portions glass wool. Cooling was effected by a stream of water (temperature 8–10°) flowing through the platinum tube, the velocity being maintained at about 1.5 litres per minute, and also by immersion of the whole cell in a bath at the same temperature.

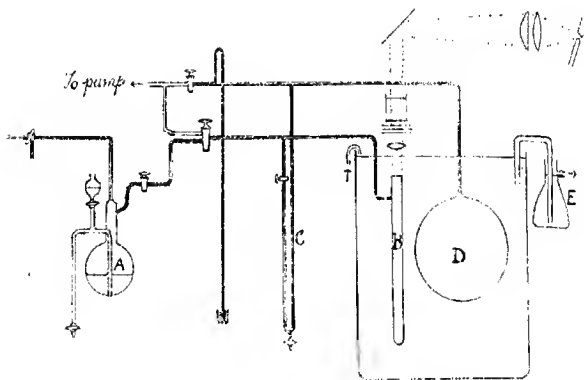
Using, as recommended by Fischer and Massenez (*loc. cit.*), an acid of density 1.085 as electrolyte and an anodic current density of approximately 45 amperes per sq. cm., corresponding with a current of 1.3 amperes, no difficulty was experienced in obtaining an ozone concentration of 17 per cent. by weight (11 per cent. by volume). The ozonised oxygen rising from the anode was collected in a small glass bell and conveyed, by capillary tubing, either to a reservoir in which it could be stored over concentrated sulphuric acid or through an absorption tube for analysis. From time to time the gas given by this apparatus was analysed and was found to be of almost unchanged composition, 16.8 to 17.1 per cent. of

ozone.* This was the concentration of ozone employed in most of the experiments to be described.

The remainder of the apparatus is shown in the figure.

From the gas reservoir, *A*, the ozone was transferred to the experimental tube, *B*, of dimensions 40 cm. in length, 1.8 cm. in diameter, and capacity 107 c.c., which stood vertically in a glass thermostat. The sulphuric acid manometer, *C*, made of capillary tubing of 1 mm. bore, was connected as shown with the tube, *B*, and the compensator, *D*, a glass balloon of 1 litre capacity, immersed in the thermostat. Finally, the whole apparatus was joined to mercury- and water-pumps, through a tube containing potassium hydroxide, which served the purpose of decomposing the ozone as

FIG. 1.



it was pumped out, thereby preventing its attacking the mercury of the pump. The apparatus was constructed entirely of glass, and the gas came into contact only with glass, sulphuric acid, and, to a slight extent, with glacial phosphoric acid used for lubricating the taps. Before being sealed to the rest of the apparatus, the reaction tube, *B*, was treated with chromic acid mixture, rinsed with distilled water, and dried, care being taken to exclude particles of dust. This was rendered necessary since Warburg (*Ann. Physik*, 1902, [iv], 9, 1286) found that ozone decomposes very slowly at

* At a late stage in the work, damage to the anode necessitated the making of a new and possibly less efficient one. This, together with a higher temperature of the water used for cooling, resulted in a lower ozone concentration—13 per cent.—and a few experiments were made with this ozone.

the ordinary temperature in the dark, but that the rate may be much increased by traces of foreign matter, which acts catalytically in promoting the unimolecular reaction $O_3 \rightarrow O_2 + O$. He showed that the velocity of deoxygenation is apparently independent of the nature of the agent used to dry the gas and that, in the tubes most free from dust particles, the ozone concentration fell only from 8 per cent. to 7.5 per cent. in the first 100 hours, at room temperature. Experiments carried out with the tube *B*, whilst showing a greater decomposition than this, proved that the amount of "catalytic dark decomposition," in all cases, was too small to affect the results obtained during the time the tube was illuminated. Thus the maximum "dark decomposition" ever observed corresponded with an increase of pressure of 5.4 mm. of sulphuric acid in 220 minutes. This maximum, which was far higher than the average amount of "dark decomposition," corresponds with a quantity approaching the order of the experimental error in reading the manometer, when reduced to the time taken for an experiment in which the tube was illuminated. Weigert (*loc. cit.*), in an investigation on the decomposition of ozone by ultra-violet light, observed a much greater decomposition in the dark, but this is probably due to the fact that his ozone was in contact with paraffin and also with sulphuric acid.

The source of illumination used was a hand-regulated carbon arc projection lamp, consuming 30–35 amperes. The horizontal beam formed by two lenses was reflected vertically downwards by a plane mirror. It then passed through a layer of water, the thickness of which could be varied, two thick plates of crown glass (total thickness 3.2 cm.) and a double convex lens. Before entering the experimental tube it traversed a further layer of water, the depth of which could be adjusted by altering the level of the syphon, *E*. The intensity of the light of the carbon arc leaves much to be desired in point of constancy and, as a source of illumination for photochemical work in general, it is not very suitable; but, as the main purpose of this investigation was to establish qualitatively the decomposition of ozone in visible light, this disadvantage was outweighed by the strong intensity obtainable. By observing certain precautions, however, such as carefully regulating the distance between the poles so as to maintain a constant current strength, it was found possible to avoid large and sudden irregularities in the intensity of the light, but it is difficult to remedy the gradual change in the light due to movement of the position of the positive crater. During an experiment, a vigorous stream of water, either direct from the town supply or from an auxiliary thermostat, was passed through the main

thermostat in order to maintain a constant temperature in the reaction tube. The temperatures employed in different experiments varied between 8° and 30°.

When the tube containing 16—17 per cent. of ozone at atmospheric pressure was illuminated, the beam appeared of a slight but distinct blue colour, indicating absorption of the less refrangible portion of the spectrum. This has previously been observed by several workers, among whom mention may be made of Liveing and Dewar (*Phil. Mag.*, 1888, [v], 25, 286), although they state that the absorption bands of ozone in the visible part of the spectrum are extremely faint.

On exposure of the experimental tube containing ozone to light, the following changes in the pressure were observed. The pressure first increased rapidly for about fifteen seconds, then rose steadily, but more slowly; finally, on cutting off the light, the pressure fell, attaining in four minutes a constant value, which corresponded with a certain amount of decomposition of ozone. This result is due to a heating effect caused by absorption by the ozone of certain parts of the visible spectrum, the energy of which is converted into infra-red radiation. By the use of a light of constant intensity, after fifteen to twenty seconds, a stationary thermal state is reached when the amount of heat flowing out from the tube to the thermostat, maintained at constant temperature, is equal to that being generated by the absorption. The further, slower increase of pressure is that due to decomposition of ozone. When the light is turned off, the pressure again decreases as the temperature of the contents of the tube falls to that of the thermostat. Thus, in one experiment, the following figures were obtained:

Temperature of thermostat = 10°. Barometric pressure = 758 mm. Manometric difference at the start, 1.6 mm. of sulphuric acid. Manometric difference after five minutes' illumination, 20.4 mm. of sulphuric acid.

The light was then cut off and the manometer read after the lapse of a further five minutes.

Final manometric difference, 9.3 mm. of sulphuric acid. We therefore obtain as the increase of pressure due to decomposition of ozone during illumination for five minutes, $9.3 - 1.6 = 7.7$ mm. of sulphuric acid, and an increase of pressure due to heating of the ozone, $20.4 - 9.3 = 11.1$ mm. of sulphuric acid.

From the latter increase of pressure may be calculated the average rise of temperature in the tube. In this case the value obtained is 0.5°.

Table I shows one series of results out of many obtained by illuminating the experimental tube for successive intervals of five

minutes and interpreting the observed manometric differences in the manner indicated in the above calculation.

TABLE I.

Temperature = 10°. Pressure = 768 mm. Ozone concentration = 11 per cent. by volume.

p_0	p	$p - p_0$	p'	$p' - p$	ΔT
1.7	13.4	11.7	29.3	15.9	0.79°
13.4	23.2	9.8	34.2	11.0	0.55
23.2	31.2	8.0	41.5	10.3	0.52
34.8	41.7	6.9	53.6	11.9	0.59
41.7	49.9	8.2	62.4	12.5	0.62
50.3	57.8	7.5	68.8	11.0	0.55

Where p_0 = the initial difference of pressure, before illumination, in mm. of sulphuric acid; p = the final difference of pressure after attainment of thermal equilibrium; p' = the difference of pressure immediately before cutting off the light; ΔT = the mean rise of temperature of the gas above the temperature of the thermostat.

The increase of pressure (column $p - p_0$) corresponding with total decomposition of the ozone present = 317 mm. of sulphuric acid.

These results show that, with the light employed, ozone undergoes decomposition and that the extent of decomposition, in equal intervals of time, is as nearly constant as could be anticipated from the nature of the source of the light.

In all our experiments in which decomposition of ozone was indicated, this heating effect (column ΔT) was observed. Its extent depended on the intensity of the light, but was usually of the order of 0.5°. This was the average rise of temperature of the ozonised oxygen during illumination, and it is, of course, in itself insufficient to account for the observed rate of decomposition. The possibility remained, however, that the gas near the centre of the tube might be at a far higher temperature, sufficiently high, in fact, to account for the decomposition by the bimolecular, thermal reaction $2O_3 \rightarrow 3O_2$, which has been studied by Warburg (*loc. cit.*), Clement (*Ann. Physik*, 1904, [iv], 14, 342), and Chapman and Jones (T., 1910, 97, 2463). That this, in all probability, is not so may be shown in the following way. During illumination the gas is heated owing to the absorption of light, the outside of the tube is maintained at a constant temperature, and the internal temperature increases from T_0 , at the outside, to T_{max} , the temperature at the centre. As only a small fraction of the light is absorbed, we may consider that the intensities of the incident and emergent beams are practically identical and therefore (with

constant intensity of light) the temperature at any point of the tube is dependent only on the distance from the axis and is independent of the distance from the ends. Also consider that the whole cross-section of the tube is illuminated at equal intensity, that no convection occurs, and that heat flows only at right angles to the length of the tube. With these assumptions, it can readily be shown that the maximum rise of temperature is double the mean rise. This is necessarily the highest temperature which the hottest part of the gas can attain, as convection, which undoubtedly occurs, tends to decrease this value. The largest mean rise of temperature observed in these experiments amounted to 0.8° (see Table I), and thus the maximum rise was, at the most, double this or 1.6° . It may be calculated from Warburg's results for the rates of the bimolecular decomposition of ozone at different temperatures that in order to account for the observed velocity of deoxygenation in this experiment, the whole of the gas would have to be at a temperature between 80° and 90° . It is therefore entirely justifiable to assume that the slight warming which the gas undergoes on illumination is not the cause of its decomposition, and that the latter is due to the light employed.

As stated above, the beam from the carbon arc passed through several thicknesses of glass and through a layer of water before entering the ozonised oxygen, in order that most of the ultra-violet and infra-red portions of the spectrum might be removed. By means of photographs taken on a Hilger quartz spectrograph, it was found that the glass screens deprived the beam of light from the arc of all that portion of the spectrum of wave-lengths shorter than $330 \mu\mu$.^{*} The conclusion that ultra-violet light is not responsible for the photochemical decomposition of ozone observed in these experiments is further supported by the fact that the rate of decomposition was not sensibly diminished by interposition, between the source of the light and the tube, of an aesculin filter, which transmitted only wave-lengths longer than $380 \mu\mu$.

The other limit to the wave-length of the effective light entering the experimental tube is obtained from a consideration of the absorption of water in the extreme red portion of the visible spectrum. According to Nicholls (*Physical Rev.*, 1894, 1, 1), the value of the absorption coefficient α for water is 0.272 at $779 \mu\mu$, and this increases with increasing wave-length. The absorption coefficient is defined by the equation

$$I = I_0 e^{-\alpha d}.$$

^{*} For his kindness in taking these photographs, we have to thank Mr. L. W. Codd.

in which I_0 = the intensity of incident light of a given wave-length.

I = the intensity of emergent light of the same wave-length.

d = the thickness of the water layer in centimetres.

It follows, from Nicholls's value, that the fraction of light of wave-length $779 \mu\mu$ transmitted through a layer of water 1 cm. in thickness is 0.76 and that through 10 cm. of water only 0.066. Hence, if wave-lengths of this order were effecting the decomposition of ozone, it would be anticipated that the rate of decomposition would vary with the thickness of the water screen through which the light passed. Experiments undertaken to test this point showed that no such effect was produced. The results of two such experiments, in which the times of illumination were five minutes, are given in Table II.

TABLE II.

	Thickness of water layer.	p_0 .	p .	p	p_0 .
Expt. I.	1 cm.	1.5	5.0	3.5	
	10 "	5.0	8.3	3.3	
Expt. II.	1 "	13.2	19.9	6.7	
	10 "	19.9	25.6	5.7	

Within the experimental error, the rates of decomposition are independent of the thickness of the water screen, and, in consequence, it may be assumed that light of wave-length longer than $770 \mu\mu$ was not causing the decomposition of ozone in these experiments.

We therefore draw the conclusion that light of wave-lengths between $400 \mu\mu$ and $780 \mu\mu$, that is, light of the visible portion of the spectrum, is capable of decomposing ozone.

The problem of further narrowing the effective limits of the spectrum presented some difficulty. Filters of aqueous solutions of inorganic salts were examined, but were found, in most cases, to be useless, as either the limits of transmission were not definite enough or, where the selection was better, the light transmitted was too feeble to effect any decomposition during a convenient interval of time. The filters finally employed were gelatin film filters obtained from Messrs. Kodak, Ltd., the percentage transmission of each filter, at a given wave-length, being taken from tables supplied by the makers. It was not possible to verify these figures, as a spectrophotometer was not available; the limits of visible transmission, however, were checked, for each filter, on a Hilger wave-length spectrometer and were found to agree with what would be anticipated from the maker's tables. Each filter was mounted between glass plates and placed so as to permit

cooling by the water flowing around and over the experimental tube.

The method of working was as follows. The amount of decomposition of ozone produced in a given time by light transmitted through one of the filters was compared with that effected, in the same time, by white light of the same intensity. As the intensity of the light tended to be variable, this comparison was made on the results of three successive experiments; in the first and the third white light was used, and in the second the filter was interposed. The amount of decomposition registered manometrically in the second experiment was compared with the mean of the other two. Experiments in which the results of the first and the third varied by more than 40 per cent. of the larger reading were rejected. The results obtained in this manner are shown in Table III.

TABLE III.
Percentage decomposition of ozone.

Filter A.	Filter B.	Filter C.*	Filter D.	Filter E.*
17	24	40	70	10
22	25	44	86	
20	32		85	
	37		71	
	39		71	
	36		88	
	42		85	
	37		73	
			76	
Mean	20	42	78	10

* The transmissive power of these filters was affected by the strong light employed and, in consequence, no further experiments could be carried out with them.

The figures in the table are percentage decompositions effected by light transmitted through the corresponding filters compared with that caused by white light of the same intensity, under the same conditions. Table IV gives the percentage transmissions of these filters at various wave-lengths as determined by the makers, Messrs. Kodak, Ltd., and published in their booklet "Written Light Filters."

From the figures given in Tables III and IV the following conclusions may be drawn.

(1) Light of the extreme red portion of the visible spectrum is capable of decomposing ozone. The head of this active band must lie between 670 and 760 $\mu\mu$, since light transmitted through filter A effects 20 per cent. of the decomposition caused by the whole of the visible spectrum and it is only at wave-lengths longer than

TABLE IV.

Wave-length. $\mu\mu$.	Filter A. (70).	Filter B. (29).	Filter C. (32).	Filter D. (12).	Filter E. (43).*
400			49.0		63.2
490			20.2	0.3	54.0
510			4.0	28.0	50.0
590			Nil.	87.0	1.0
600			6.4	88.0	
610		0.4	34.0	89.0	
620		13.8	63.0	89.0	
650	0.4	63.6	73.0	91.0	
670	19.6	69.0	70.0	92.0	
680	34.0	70.0	68.0	93.0	
700	45.5	71.5	65.0	94.0	

* The numbers in brackets at the heads of the columns of percentage transmissions are the makers' numbers for the filters.

670 $\mu\mu$ that the transmission reaches 20 per cent. The effect of interposition of this filter was examined with especial care, and experiments with it were carried out over time intervals longer than five minutes, in one case above half an hour. In all cases the extent of decomposition was found to be approximately proportional to the time of exposure and about 20 per cent. of that observed with white light.

(2) Light of wave-lengths between 615 and 510 $\mu\mu$ is effective in causing decomposition of ozone. It is considered improbable that light of wave-lengths between 670 and 615 $\mu\mu$ is causing deoxygenation, since the decomposition obtained by the use of filter B, which transmits in this region, is only so much in excess of that obtained with filter A, as would be expected from its (B's) increased transmission of light of wave-length longer than 670 $\mu\mu$. The high percentage decomposition obtained with light transmitted through filter D indicates that a second band of light is also causing deoxygenation, since the light present of wave-length longer than 670 $\mu\mu$ is now insufficient to account for the observed result. The average transmissions of filters A and D to light of wave-lengths between 670 and 700 $\mu\mu$ are in the ratio of 40 to 90, whereas the percentage decompositions observed with each are in the ratio of 20 to 78. The limit of 510 $\mu\mu$ is set to one end of this active band by the low transmission of filter D to shorter waves than those of this value. The other end of the band is defined by the results obtained with filter C. Light transmitted by this filter effects a slightly greater percentage decomposition than that transmitted by filter B, although the latter allows more light of wave-lengths longer than 670 $\mu\mu$ to pass through. It may be inferred from this result that part of the second active band is transmitted by

filter C, but is absorbed by filter B. Hence it follows that the longer limit of this band must lie between 620 and 610 $\mu\mu$.

(3) As regards the effect of the remaining portion of the visible spectrum, namely, that of wave-lengths between 400 and 510 $\mu\mu$, no definite inference can be drawn from the data. The use of filter E, which transmits in this region, is accompanied by a small decomposition of the ozone. Since, however, this filter transmits 10 per cent. of the energy of the incident light of wave-length 550 $\mu\mu$, and more of that of shorter wave-lengths, it is possible to account for the observed decomposition by assuming it to be due to light of wave-lengths between 550 and 520 $\mu\mu$, which is also transmitted by filter D. Consequently we incline to the opinion that if light of wave-lengths between 510 and 400 $\mu\mu$ is capable of causing deozoneisation, its activity is very small in comparison with that of either of the two active regions already discussed, namely, 760 to 670 $\mu\mu$ and 615 to 510 $\mu\mu$.

Discussion of Results.

We may compare the results given above for the photochemically active portions of the visible spectrum with the absorption spectrum of ozone, which has been determined by Chappuis (*Compt. rend.*, 1880, 91, 935; 1882, 94, 858), Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.*, 1906, 4, 125) and others. Chappuis employed a tube containing ozonised oxygen, prepared by the silent discharge method, and found eleven absorption bands in the visible region. The band of longest wave-length was located at 629 $\mu\mu$, and the two most intense on either side of the sodium line, the one between 609.5 and 593.5 $\mu\mu$, the other between 577 and 560 $\mu\mu$. Both the characteristic bands are also shown by the blue liquid ozone. Of the bands found by Chappuis, four, including the two most intense, lie in the region between 520 and 615 $\mu\mu$, which has been found by us to be one of the regions effective in causing decomposition of ozone. As regards the relative effectiveness of the light at each of these four bands, nothing can be said at present. It may be that the light energy of wave-length corresponding with one of the bands alone is used in activating the ozone molecule, that of the others being converted into heat, or it may be that all the bands contribute, to some extent, to the decomposition. Luther (*Zeitsch. Elektrochem.*, 1908, 14, 447) has expressed the opinion that in photochemical reaction all the absorbed wave-lengths are chemically effective, but, in many cases, the results are not noticeable.

No absorption bands appear to have been found for ozone in the region of wave-lengths 760 to 670 $\mu\mu$, which has been found

by us to be photochemically active. However, Ladenburg and Lehmann (*loc. cit.*), using a gas containing a very high percentage of ozone, prepared by the Goldstein (E. Goldstein, *Ber.*, 1903, **36**, 3042) method, found, in addition to the bands observed by Chappuis, "general" absorption extending over the region of wave-lengths longer than $500\ \mu\mu$. It therefore seems probable that the photochemically effective portion of the spectrum between 670 and $760\ \mu\mu$ lies in this region of "general" absorption.

Summary.

1. The action of light of the visible spectrum on ozone has been investigated.

2. At room temperature, ozonised oxygen, containing 16 per cent. (by weight) of ozone, is deozonised by the action of intense light of wave-lengths between 400 and $800\ \mu\mu$.

3. Reasons are given to show that the slight heating which the gas undergoes is not the cause of the decomposition.

4. The use of light filters indicates that the effective regions of the spectrum lie between (a) 760 and 670 $\mu\mu$ and (b) 615 and 510 $\mu\mu$.

In conclusion, we desire to express our thanks to Professor W. C. McC. Lewis, who suggested this work, for advice during its course.

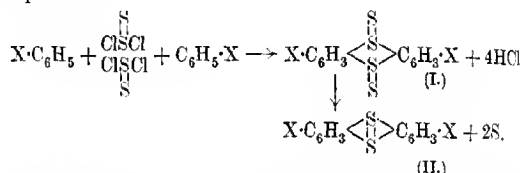
THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
THE UNIVERSITY OF LIVERPOOL. [Received, October 4th, 1921.]

CCXXIII.—Syntheses in the Thianthren Series. Part I.

By JÑANENDRA NATH RÂY.

THE present investigation was undertaken with two objects in view, first, to ascertain the extent of the applicability of aluminium amalgam as a condensing agent, and, secondly, to develop a convenient method of synthesising thianthren derivatives, which appear to have been very little investigated. Fries and Engelbertz (*Annalen*, 1915, **407**, 194) failed to prepare dimethoxythianthren directly, which, however, was obtained from the corresponding diazosulphide by heating. Such a procedure is undoubtedly tedious, and therefore a systematic investigation seemed desirable.

[Cohen (T., 1899, 75, 887) condensed sulphur chloride with benzene and toluene by means of the aluminium-mercury couple, but in the case of the higher hydrocarbons the products were uncrystallisable oils which decomposed on distillation. In the present paper, compounds containing acetyl-amino-, chloro-, methyl-, nitro-, nitroacetyl-amino-, acid chloride, keto-, and aldehyde-groups are described. It has been found that the reaction is inhibited by a nitro-group in the molecule, as no products could be isolated either under ordinary conditions or at high temperatures. The reaction with an iodo-compound is an interesting one, and will be dealt with subsequently. Usually, two molecules of sulphur chloride react with two molecules of the substance. Since the ortho-position of the sulphur atoms in thianthren has been proved (Deuss, *Ber.*, 1908, 41, 2329), the reaction may be assumed to take place thus :

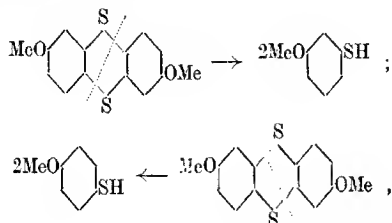


The intermediate compound (I) has actually been isolated. It is very unstable and suffers decomposition with moisture, liberating free sulphur. This compound is coloured, but on decomposition into the thianthren derivative the intensity diminishes and the product is only slightly coloured. These compounds all develop an intense coloration with sulphuric acid, which is discharged on dilution with the precipitation of the compound. Evidently, a sulphonium salt analogous to the intermediate compound I is formed (compare Fries and Volk, *Ber.*, 1909, 42, 1170).

From acetanilide, diacetylaminothianthren was formed, from which the free amine was prepared by hydrolysis. This amine was diazotised and the product coupled with a few phenols and naphthols, but the dyes obtained showed no distinctive advantage over the corresponding benzene derivatives. This subject will be dealt with in a subsequent paper.

It was found in the course of this investigation that condensation between a hydrocarbon and an acid chloride cannot be effected by aluminium amalgam and that this catalyst is without action on acid chlorides. Therefore, it has been possible to condense benzoyl chloride with sulphur chloride, and the corresponding acid chloride of thianthrendicarboxylic acid has been isolated as the product.

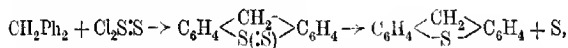
Phenolic ethers do not suffer hydrolysis, as with aluminium chloride, but the product of condensation in the case of anisole is an uncrystallisable oil. This oil gives the characteristic coloration with sulphuric acid, but breaks down into a mixture of two mercaptans on distillation. This behaviour has been found to be general in the series (compare Cohen, *loc. cit.*). Thus, in the case of anisole,



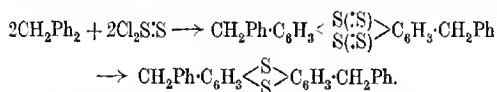
the decomposition products afford a clue to the constitution of the thianthren derivative.

In the case of iodobenzene, complete separation of iodine takes place on mixing the constituents in the presence of the catalyst, but without it, iodine is not liberated even after boiling for many hours. Thianthren is isolated in small yield, but the greater part of the material is resinified.

Sulphur chloride was condensed with diphenylmethane in the expectation of getting thioxanthen,



but the corresponding dibenzylthianthren was obtained instead :



It may be pointed out that the unsymmetrical constitution of sulphur chloride is demonstrated by the formation of thianthren (a compound of settled constitution) from benzene and sulphur chloride, for without the assumption of complicated tautomerism and rearrangement in the molecule the reaction can be explained in no other way than that depicted in this paper. Böeseken and Koning (*Rec. trav. chim.*, 1911, 30, 116) studied the behaviour of sulphur chloride in the presence of aluminium chloride to ascertain its constitution, but they drew the conclusion that a clear picture of the reaction is impossible owing to its being obscured by side-reactions. The reaction in the presence of the aluminium-mercury

couple is, however, a simple one (Cohen, *loc. cit.*), uninfluenced by concurrent reactions, and therefore the isolation of thianthren as the principal product is strong evidence in favour of the unsymmetrical constitution of sulphur chloride.

Böeseken and Koning (*loc. cit.*) found that *pp'*-dichlorodiphenyl sulphide and disulphide are the products of the reaction between chlorobenzene and sulphur chloride. The product in the present investigation is dichlorothianthren. Evidently, an entirely different course of reaction is induced by the two catalysts, aluminium chloride and aluminium amalgam.

EXPERIMENTAL.

The method of condensation was as follows. The substance was dissolved in dry carbon disulphide in a flask attached to a reflux condenser, through the upper end of which the sulphur chloride, dissolved in the same solvent, was added drop by drop. The catalyst, prepared from aluminium foil and dried between filter-paper, was quickly inserted into the flask before the addition of the sulphur chloride. The flask was cooled, when necessary, by immersion in water.

Condensation with Chlorobenzene: Dichlorothianthren.

A violent reaction ensued, and a bluish-green solid eventually separated when 10 c.c. of chlorobenzene, the couple prepared from 0.3 gram of aluminium, and 8 c.c. of sulphur chloride interacted in the presence of about 10 c.c. of carbon disulphide as diluent. After remaining for two hours, the mixture was warmed at 40° for two hours, and then decanted from the amalgam on to crushed ice. The product was collected, crystallised from glacial acetic acid, the crystals were dissolved in benzene and refluxed with copper powder to remove traces of sulphur, and the substance was finally twice crystallised from acetic acid, when it was obtained in needles, melting at 147°. It gave a bluish-violet coloration with sulphuric acid (Found: Cl = 25.7; S = 22.98. Calc., Cl = 24.99; S = 22.4 per cent.). Fries and Volk (*Annalen*, 1911, 381, 312) gave 171° as the m. p. of 4:4'-dichlorothianthren, and their compound developed a deep blue colour with sulphuric acid. Possibly this compound is an isomeride.

Oxidation.—One gram of the substance was dissolved in glacial acetic acid and oxidised with boiling chromic acid mixture. The product was separated in the usual way. The sulphone crystallised from hot dilute acetic acid in needles, m. p. above 225° (Found: S = 18.5. $C_{12}H_6O_4Cl_2S_2$ requires S = 18.3 per cent.

Isolation of the Intermediate Compound.—The bluish-green solid separating from the reaction mixture was filtered and repeatedly washed with carbon disulphide, moisture being excluded. It was dried by pressing on a clean porous plate (Found: S = 37.2. $C_{12}H_6Cl_2S_4$ requires S = 36.6 per cent.).

Dichlorodimethylthianthren.

o-Chlorotoluene (5 c.c.) was condensed with 3.5 c.c. of sulphur chloride diluted with 10 c.c. of carbon disulphide. The reaction was instantaneous, and a greenish-black colour developed. The reaction was allowed to proceed at the ordinary temperature for two hours, the mixture was then heated on the water-bath for an hour, the product poured on crushed ice, and the reddish-brown, viscous mass extracted with boiling acetic acid containing a trace of water. The compound, which crystallised from the cold filtrate, was freed from sulphur by copper powder, and was dissolved in the minimum amount of chloroform and precipitated by pouring the solution into alcohol. After being then twice crystallised from acetic acid, it melted at 145° and developed a beautiful emerald-green coloration with sulphuric acid, which changed to blue on keeping (Found: Cl = 22.41; S = 21.0. $C_{14}H_{10}Cl_2S_2$ requires Cl = 22.68; S = 20.44 per cent.).

Oxidation with Nitric Acid: Preparation of the Sulphone.—The substance was heated on the water-bath with nitric acid and precipitated by water. The precipitate was crystallised from a boiling mixture of water and acetic acid. The sulphone melts and decomposes at a high temperature (Found: S = 16.85. Calc., S = 16.99 per cent.).

4 : 5-Dichloro-1 : 8-dimethylthianthren.

p-Chlorotoluene (5 c.c.) was condensed with 3.1 c.c. of sulphur chloride diluted with 10 c.c. of carbon disulphide, the reaction being moderated by cooling; eventually a greenish-black solid was produced. The reaction was allowed to proceed at the room temperature for two hours. When it slackened, the mixture was heated on the water-bath for an hour, and the product decomposed with crushed ice. The white solid thus obtained was crystallised from boiling xylene and freed from sulphur in the usual way. The substance is only slightly soluble in xylene, chloroform, acetone, or ether. It melts at $195\text{--}197^\circ$, and does not develop a coloration with sulphuric acid, probably owing to steric hindrance, as the positions 1, 4, 5, and 8 contiguous to the sulphur atoms are occupied

(Found: Cl = 22.39; S = 20.90. $C_{11}H_{10}Cl_2S_2$ requires Cl = 22.68; S = 20.44 per cent.).

The sulphone obtained on oxidation with nitric acid melts and decomposes above 250°.

Condensation of α -Chloronaphthalene and Sulphur Chloride.

α -Chloronaphthalene (2 c.c.) was condensed with 2 c.c. of sulphur chloride, and the product treated in the usual way. The resulting compound was crystallised from boiling glacial acetic acid containing a few drops of water. It melted at 64° (Found: Cl = 18.2; S = 17.2. $C_{20}H_{10}Cl_2S_2$ requires Cl = 18.4; S = 16.6 per cent.).

Diacetylaminothianthren.

Ten grams of acetanilide dissolved in 15 c.c. of carbon disulphide were treated with the calculated amount of sulphur chloride (2 mols.). The reaction was started by heating on the water-bath and the mixture boiled for four hours until the reaction was completed. The product, isolated in the usual way, was crystallised from boiling alcohol and from boiling dilute acetic acid until it was pure, when it melted at 198–200°. This compound gave a buff coloration with sulphuric acid (Found: N = 8.56; S = 19.8. $C_{16}H_{14}O_2N_2S_2$ requires N = 8.48; S = 19.39 per cent.).

The acetyl compound was hydrolysed with hydrochloric acid, and the diamine liberated with alkali. It crystallised from alcohol in canary-yellow needles, m. p. 102–104° (Found: N = 11.5; S = 26.8. $C_{12}H_{10}N_2S_2$ requires N = 11.3; S = 26.01 per cent.).

The diamine was diazotised and the product coupled with the naphthols. The α -naphthol compound is scarlet, melts at 104°, and gives a deep violet colour with sulphuric acid.

Dimethoxythianthren.

Five c.c. of anisole were condensed with 4 c.c. of sulphur chloride. The reaction was completed on the water-bath after the evolution of hydrogen chloride had moderated. A viscous, heavy, red oil (A) was obtained on decomposition of the product with ice. This was shaken with sodium hydroxide solution to extract any phenolic compound, the unchanged anisole removed by distillation with steam, the residu dissolved in benzene, and the free sulphur removed with copper powder. The benzene solution deposited an oily substance which gave a beautiful green coloration with sulphuric acid.

The oil (A) was distilled at slightly diminished pressure, and an

oil passed over at 175—185°. This oil is a mercaptan, because it gives a compound with mercuric chloride, dissolves in sodium hydroxide solution, and is oxidised by iodine. The distillate was oxidised with chromic acid mixture, or, better, with potassium permanganate to sulphonic acids, the sodium salts of which were isolated in the usual way. They were converted into the amides through the chlorides. The amides were crystallised from hot water, in which one, m. p. 116°, was sparingly soluble. The aqueous filtrate was evaporated to dryness; the residue, after crystallisation from alcohol, melted at 126—128°. Gatterman (*Ber.*, 1899, **32**, 1154) gives the m. p. of *m*-methoxybenzenesulphonamide as 128° and that of the *para*-compound as 116°. Therefore the foregoing oil is a mixture of *m*-methoxyphenyl mercaptan and *p*-methoxyphenyl mercaptan.

Condensation with Phenetole.

Phenetole was similarly condensed with sulphur chloride. A viscous, red oil, as in the case of anisole, was obtained, which yielded mercaptans on distillation; the mixture, however, has not yet been identified.

Diacylthianthren.

Five c.c. of acetophenone mixed with 5 c.c. of sulphur chloride were diluted with 10 c.c. of carbon disulphide and the couple was quickly added. The liquid became deep red and a vigorous reaction ensued. After the violence of the reaction had abated, the mixture was warmed for an hour and then boiled for fifteen minutes on the water-bath. The product was decomposed with ice and the viscous mass obtained was freed from sulphur and repeatedly crystallised from a mixture of chloroform and alcohol. Diacylthianthren melts at 88—91°, forms a phenylhydrazone (which melts with decomposition), develops a red coloration with sulphuric acid, and yields benzoic acid on oxidation with nitric acid (Found: S = 21.6. $C_{16}H_{12}O_2S_2$ requires S = 21.3 per cent.).

Dibenzylthianthren.

Diphenylmethane (2.2 grams) was condensed with 1.2 c.c. of sulphur chloride, carbon disulphide being slowly added during the reaction. The product, after decomposition with water, was freed from carbon disulphide and sulphur and crystallised from boiling diluted alcohol, when it melted at 196°, and gave a beautiful greenish-red fluorescence with sulphuric acid, which was destroyed by the addition of a trace of potassium nitrate (Found: C = 78.5;
3 x 2

H = 5.5; S = 16.25. $C_{26}H_{20}S_2$ requires C = 78.7; H = 5.05; S = 16.16 per cent.). Thioxanthen melts at 128° and gives no fluorescence with sulphuric acid (Graebe, *Annalen*, 1891, 263, 14).

Condensation with Iodobenzene: Formation of Thianthren.

Iodobenzene (5 grams), dissolved in 10 c.c. of carbon disulphide, was slowly treated with 2 c.c. of sulphur chloride. Instantaneous separation of iodine took place. The reaction was completed by warming on the water-bath, and the product was poured into an ice-cold solution of sodium hydroxide. The precipitated resinous mass was freed from the last traces of iodine by sodium hydrogen sulphite and the white residue was extracted with boiling acetone. The acetone solution, after being concentrated, deposited crude thianthren, which was crystallised from alcohol. It then melted at 160° (mixed m. p. with thianthren, 160°), and gave the violet coloration with sulphuric acid characteristic of thianthren. During the first stage of the reaction, chlorine was evolved together with hydrogen chloride, but the evolution ceased during the progress of the reaction.

Iodobenzene and aluminium amalgam were warmed on the water-bath and refluxed with carbon disulphide for many hours without any change occurring. Sulphur chloride and iodobenzene were similarly heated on the water-bath without reacting. When, however, the amalgam was dropped into a mixture of sulphur chloride and iodobenzene, a vigorous reaction immediately began, with the instantaneous separation of iodine. The amount of iodine liberated roughly corresponded with that present in the iodobenzene.

Thianthrenedicarboxylic Acid.

Three c.c. of freshly-distilled sulphur chloride were condensed with 2 c.c. of freshly-distilled benzoyl chloride by heating at 110° for two hours. The traces of unchanged constituents were removed by heating in a current of dry air, and the product was decomposed with ice and extracted with a dilute solution of sodium hydroxide, from which it was precipitated by dilute hydrochloric acid. The precipitate was crystallised from boiling water to which a little alcohol had been added. Pale yellow leaflets appeared while the liquid was still hot. The solution was filtered without cooling. The thianthrenedicarboxylic acid crystallised in flakes, m. p. 204° (Found: S = 21.2. $C_{14}H_8O_4S_2$ requires S = 21.05 per cent. Found: in the barium salt, Ba = 31.1. $C_{14}H_6O_4S_2Ba$ requires Ba = 31.2 per cent.), gave a pink coloration with sulphuric acid, and lost

carbon dioxide when it was melted and kept at 210° for some time; the cold mass crystallised from a mixture of chloroform and alcohol and was identified as thianthren.

Attempts to condense sulphur chloride with *p*-benzoquinone, ethyl benzoate, or nitrobenzene in the presence of aluminium amalgam were unsuccessful. In the case of *p*-iodotoluene, the iodine was entirely eliminated, but the product was resinous and resisted all attempts to crystallise it.

My best thanks are offered to Sir P. C. Ray, Dr. P. C. Mitter, and Dr. H. K. Sen for the interest they have taken in the work.

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[Received, August 23rd, 1921.]

(CCXXIV).—*The Solubility of Glucinum Sulphate in Water and Sulphuric Acid at 25° .*

By HUBERT THOMAS STANLEY BRITTON.

THE solubility of glucinum sulphate in water and in sulphuric acid of varying concentrations was investigated at 25° by Wirth (*Zeitsch. anorg. Chem.*, 1913, **79**, 307). His investigations were carried out by allowing glucinum sulphate hexahydrate to attain equilibrium at 25° with the liquid phase. In this way, he found 1.96 grams of glucina in 100 grams of aqueous solution, but when the estimation was carried out by first raising the temperature of the mixture and then allowing it to attain equilibrium at 25° , 1.984 grams of glucina were found. From Wirth's data, it appears that the stable solid phase in equilibrium with aqueous solutions and with solutions in sulphuric acid of concentrations up to thirteen normal is the hexahydrate; above such concentration the tetrahydrate becomes the stable solid phase. This is contrary to the author's experience, for whenever crystals of glucinum sulphate have been prepared, either from aqueous or sulphuric acid solutions of varying concentration, they have invariably been the tetrahydrate. If, however, care is not taken to reduce the amount of ammonia adsorbed by the glucinum hydroxide before dissolving in sulphuric acid, crystals of glucinum ammonium sulphate will result (*vide* this vol., p. 1465).

Moreover, Wirth found that the solubility of glucinum sulphate

in equilibrium with the hexahydrate was only 8.212 grams of glucinum sulphate in 100 grams of solution, whereas the author found that 100 grams of solution saturated with respect to the tetrahydrate contained 29.94 grams of glucinum sulphate. Incidentally, this figure appears to be in agreement with that found by Levi Malvano * at 30° (*Zeitsch. anorg. Chem.*, 1905, **48**, 452), namely, 30.5 grams. Hence, it was believed that at the ordinary temperature the stable solid phase was the tetrahydrate, and consequently if a metastable hydrate exists at such temperature, the amount of glucinum sulphate in solution in equilibrium with it, must be greater, and not less as found by Wirth.

Marignac (*Ann. chim. phys.*, 1873, [iv], **30**, 45) thought that he once obtained the hexahydrate by evaporating a supersaturated solution of sodium sulphate and glucinum sulphate, which, on exposure to air, effloresced. Levi Malvano (*loc. cit.*) obtained the hexahydrate from a commercial source. He states that he was only able to prepare the hexahydrate after many fruitless attempts, but that having once been prepared, the hexahydrate always crystallised from its aqueous solutions over a considerable range of temperature. Many methods, generally employed for the preparation of metastable hydrates, were adopted in trying to obtain the hexahydrate from solutions of the tetrahydrate, such as evaporation over sulphuric acid, subjection to cold and inoculation with crystals of the hexahydrate. In every case the tetrahydrate crystallised out. The successful method was to prepare a highly supersaturated solution by dissolving excess of either glucinum hydroxide or carbonate in concentrated sulphuric acid which had been slightly diluted, and then suddenly shaking at the ordinary temperature, when crystals containing six molecules of water separated out and were identical with the commercial product. They were quite stable in air. It is interesting to note Levi Malvano's observation that glucinum sulphate hexahydrate always crystallised from solutions made from it. He appears to have been under the impression that the nature of the solution varied with the hydrate ion of the crystals from which the solution was made. This he further demonstrated by stating that the glucinum oxide obtained by precipitation with ammonium sulphide from solutions of the tetrahydrate was, on ignition, white, whereas that from hexahydrate solutions was blue. If the ignition of any glucinum hydroxide precipitate together with the filter-paper

* Levi Malvano's analysis of glucinum sulphate tetrahydrate.

The data given for " SO_4 " are too high, being in reality those for " SO_3 " and as the figures given for ClO are accurate, those for H_2O are correspondingly low.

has not been sufficiently prolonged, the resulting ash is often faintly blue, no doubt due to the presence of a little carbon, for on further ignition the oxide becomes white. Parsons and Fuller (*Science*, 1906, **24**, 202) made repeated attempts to obtain the hexahydrate, but every attempt was futile, although they state that they faithfully followed Levi Malvano's instructions, besides trying other methods. Furthermore, Parsons ("Chemistry of Beryllium," 1908, p. 33) states that he obtained a bottle labelled "hexahydrate" from the dealers from whom Levi Malvano procured his supply; analysis of the contents proved them to be nothing but the regular tetrahydrate. Taboury (*Compt. rend.*, 1914, **159**, 180) was unable to prepare the hexahydrate. The author has also been unable to prepare the hexahydrate either according to Levi Malvano, or, as the following solubility determinations show, to Wirth.

EXPERIMENTAL.

Solutions of sulphuric acid of various normalities were warmed and saturated with pure glucinum sulphate tetrahydrate. They were then placed in a thermostat which had been carefully regulated at $25.0 \pm 0.1^\circ$, and mechanically stirred until equilibrium between the liquid phase and the solid phase which had crystallised out had been attained. In all cases a day's stirring was found to be sufficient; examination of the liquid phase after further periods of stirring, from one to three days, showed no further change in its composition. After the solid phase had been allowed to settle completely, exactly 20 c.c. of the clear liquid phase were pipetted into a tared beaker and weighed. These solutions were made up to 250 c.c., and aliquot portions taken for the estimation of glucinum oxide and total sulphate. From these data, the amount of glucina in 100 grams of solution and also the final concentration of the free sulphuric acid were calculated.

To ascertain the nature of the solid phases, the following procedure was adopted. They were dried as well as possible between filter-papers, and the percentage of glucina estimated by strongly heating weighed quantities to constant weight (*vide* this vol., p. 1465).

Besides allowing the solid phases to crystallise out from super-saturated solutions at 25° as in the above determinations, further determinations were made by mixing solutions of sulphuric acid with excess of glucinum sulphate tetrahydrate crystals at room temperature and again stirring until both phases were in equilibrium one with the other. Again a day's stirring was all that was found necessary.

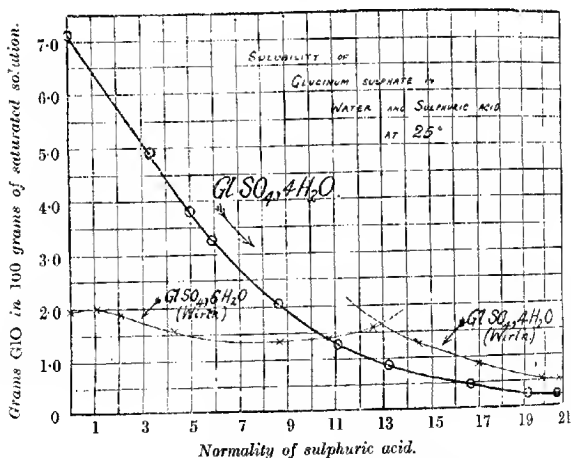
Results.

No.	Sulphuric acid.		100 Grams of saturated solution contain		Percentage of GIO in moist solid phase.*	Solid phase,* $\text{GiSO}_4 \cdot 4\text{H}_2\text{O}$
	Normality.	Percentage.	GiO.	GiSO_4 .		
1	Water	—	7.152	29.94	14.2	
2	3.39	12.91	4.900	20.51	13.5	
3	5.01	19.17	3.800	16.91	13.7	
4	5.87	22.36	3.261	13.65	13.5	
5	8.66	32.04	2.057	8.61	14.0	
6	11.10	40.34	1.254	5.25	13.1	
7	13.23	46.59	0.846	3.54	13.2	
8	16.70	55.50	0.486	2.04	13.5	
9	19.23	62.02	0.234	0.98	13.4	
10	20.65	66.07	0.213	0.89	13.2	
11	20.70	66.10	0.206	0.86	13.4	

* Compare percentage of GIO in $\text{GiSO}_4 \cdot 2\text{H}_2\text{O}$ = 17.79; $\text{GiSO}_4 \cdot 4\text{H}_2\text{O}$ = 14.17; $\text{GiSO}_4 \cdot 6\text{H}_2\text{O}$ = 11.73.

All the above results, except Nos. 4, 10, and 11, were obtained from solutions which had been saturated with glucinum sulphate at a temperature above 25° , from which it was in each case found

FIG. 1.



that glucinum sulphate tetrahydrate had crystallised. Nos. 4, 10, and 11 are the results obtained by allowing the solid phase—glucinum sulphate tetrahydrate—to attain equilibrium with solutions of sulphuric acid at 25° . These data are shown graphically in Fig. 1, using as ordinate and abscissa the same magnitudes as

were employed by Wirth. The curve obtained by Wirth is shown by the thinner lines.

Summary.

It will be seen that the curve is quite different from that obtained by Wirth. No evidence of the crystallisation of the hexahydrate from the more dilute solutions of sulphuric acid as found by Wirth has been obtained, no matter in which way the solubility determinations were carried out, and even that part of Wirth's curve which shows the composition of liquid phases in equilibrium with the tetrahydrate is somewhat higher than that represented above. From the smooth character of the curve representing solutions of glucinum sulphate in equilibrium with glucinum sulphate tetrahydrate, and from the fact that the tetrahydrate is the solid phase which is always deposited from saturated solutions under ordinary conditions, there appears to be no doubt that it is the stable hydrate. If a metastable hydrate exists, the amount of glucinum sulphate in solution in equilibrium with it being greater, the curve showing the concentrations of the solutions in equilibrium with it must lie above the curve given, which appears improbable. If the hexahydrate does exist, it appears that the conditions for its preparation have not yet been described.

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CCXXV.—*Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part IV. Aryl Derivatives of Bisiminocamphor.*

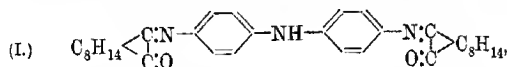
By BAWA KARTAR SINGH, MAHAN SINGH, and JIWAN LAL.

THE remarkably high molecular rotatory power displayed by products of condensing camphorquinone with aryldiamines was first noticed in connexion with *p*-phenylenebisiminocamphor (Forster and Thornley, T., 1909, 95, 941). The rotation of this compound is greatly exceeded by that of 1 : 4-naphthylenebisiminocamphor (B. K. Singh and M. Singh, T., 1920, 117, 1599), and we now find that the molecular rotatory power of *pp'*-bisiminocamphor-

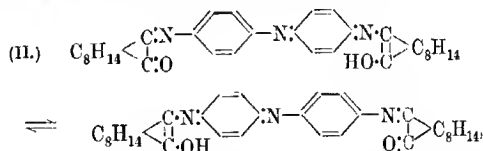
diphenylamine, prepared from camphorquinone and *pp'*-diamino-diphenylamine, is even greater, as indicated below :

	[M] _D			
	Chloro- form.	Methyl alcohol.	Ethyl alcohol.	Pyridine.
<i>pp'</i> -Bisiminocamphordiphenylamine	11385°	12375°	14231°	13288°
1 : 4-Naphthylenebisiminocamphor	8175	9052	12071	13416
<i>p</i> -Phenylenebisiminocamphor	6088	5009	5289	6173

The conventional formula for *pp'*-bisiminocamphordiphenylamine, in which the continuity of conjugated linkings is broken, suggests



an exception to the generalisation which has arisen from the study of such substances, namely, exaltation of rotatory power following concentration of conjugated linkings, azethenoid groups and benzene rings within a narrow molecular compass (Forster and Spinner, T., 1919, **115**, 889; B. K. Singh and M. Singh, *loc. cit.*). A similar anomaly is presented by camphorylamino phenyliminocamphor (Forster and Saville, this vol., p. 789), the molecular rotatory power of which exceeds that of *p*-phenylenebisiminocamphor. The case of *pp'*-bisiminocamphordiphenylamine, however, can be brought into harmony with the above generalisation by representing one of the benzene rings in the quinonoid form capable of displaying double symmetric tautomerism,



the continuity of the conjugated linkings thus becoming restored. The fluorescence to be expected from such a compound is, in this case, weak, but a hydroxyl group is indicated by the greenish-red coloration with ferric chloride.

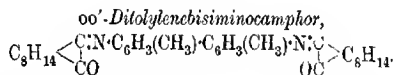
pp'-Bisiminocamphordiphenylamine is interesting also as a rare example of optically active dyes. Furthermore, it is phototropic and thermotropic, the yellow form changing to brown in sunlight; although the converse change does not occur in darkness, the brown modification rapidly becomes yellow above 75°. The remaining new compounds described in this paper, namely, *oo'*-ditolylene-

bisiminocamphor, *oo'*-dimethoxydiphenylenebisiminocamphor, and *pp'*-diphenylenebisiminocamphor, are in agreement with the above-mentioned generalisation; the first-named resembles *pp'*-diphenylenebisiminocamphor (Forster and Spinner, *loc. cit.*) in being dimorphous, but, unlike the authors quoted, we have reduced the latter substance to *pp'*-diphenylenebisiminocamphor. The effect of ortho-substitution on the rotatory power of *pp'*-diphenylenebisiminocamphor is very depressant, as indicated by the following measurements;

	[M] _D	
	Chloroform.	Methyl alcohol.
<i>pp'</i> -Diphenylenebisiminocamphor :		
(a) Yellowish-green	5472 ²	—
(b) Golden-brown	5433	5020 ²
<i>oo'</i> -Ditolylenebisiminocamphor :		
(a) Green	3929	3274
(b) Golden-yellow	4007	3462
<i>oo'</i> -Dimethoxydiphenylenebisiminocamphor ...	2003	1576

Thus the sequence of substituents in order of diminishing rotatory power is $H > CH_3 > OCH_3$.

EXPERIMENTAL.

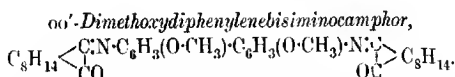


Camphorquinone (3.3 grams), tolidine dihydrochloride (2.85 grams), and excess of fused sodium acetate having been heated on the water-bath during four hours, the hard mass was extracted with 10 c.c. of cold alcohol, and the residue undissolved by water was crystallised fractionally from ether. The less soluble, preponderating component (*a*), which separated in long, green prisms, melts at 200–201°, and is readily soluble in chloroform, acetone, or hot ethyl alcohol, less so in methyl alcohol or ether; it is insoluble in cold ethyl alcohol or water (Found: $N = 5.2$. $C_{34}H_{40}O_2N_2$ requires $N = 5.5$ per cent.). The more soluble form (*b*), in golden-yellow prisms, melts at 198–199°, and is readily soluble in chloroform or acetone, less so in hot ethyl alcohol, and even more insoluble in hot methyl alcohol (Found: $N = 5.2$ per cent.). A mixture of *a* and *b* in equal amounts melts at 192–193°.

The following measurements of rotatory power, in common with all noted in this paper, are recorded as relating to the specified weight of material in 100 c.c. observed in a 2-dm. tube, the initial reading having been taken within half-an-hour :

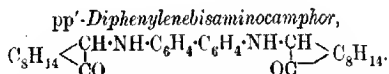
Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.1280 (a)	29°	1.98°	773°	3829°
Methyl alcohol	0.1148 (a)	30	1.48	645	3274
Chloroform	0.0564 (b)	29	0.89	789	4007
Acetone	0.2708 (b)	21	3.98	736	3738
Methyl alcohol	0.0834 (b)	29	1.14	683	3470

The foregoing rotations remained unchanged during twenty-four hours.



Camphorquinone (3.3 grams), dianisidine dihydrochloride (3.9 grams), and excess of sodium acetate having been heated on the water-bath during four hours, the residue undissolved by 10 c.c. of cold alcohol followed by water was crystallised from hot alcohol, which deposited thin, green prisms melting at 186° (Found: N = 4.84. $\text{C}_{34}\text{H}_{40}\text{O}_4\text{N}_2$ requires N = 5.18 per cent.). The substance dissolves very readily in chloroform or ether, less so in methyl alcohol and hot ethyl alcohol; it does not display mutarotation:

Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.1670	22°	1.24°	371°	2003°
Methyl alcohol	0.2635	"	1.53	290	156;



The *pp'*-diphenylenebisiminocamphor required in preparing the above product of reduction was divided into the less soluble component (a), which separated in yellowish-green prisms melting at 276°, and the more soluble component (b), forming golden-brown needles which melt at 274°, as described by Forster and Spinner (*loc. cit.*); a mixture of a and b in equal amounts melts at 267°. The substance does not display mutarotation:

Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.2370 (a)	35°	5.86°	1140°	5472°
"	0.4730 (b)	"	10.71	1132	5433
Methyl alcohol ...	0.0908 (b)	29	1.90	1046	5020

pp'-Diphenylenebisaminocamphor was produced from both modifications on agitating ethereal solutions with zinc dust and 10 per

cent. aqueous potassium hydroxide during six hours, the residue from evaporating the colourless solution being crystallised from hot alcohol, which deposited plates on cooling. The product from each source, and a mixture thereof, melted at 214° (Found: $C = 79.4$, $H = 8.28$. $C_{32}H_{40}O_2N_2$ requires $C = 79.3$; $H = 8.27$ per cent.). It is insoluble in water, but dissolves readily in chloroform or acetone; less so in methyl or ethyl alcohol.

Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.2920	17°	0.57°	97.6°	472°
Methyl alcohol	0.0650	"	0.10	76.9	372
Acetone.....	0.1435	"	0.47	163.7	792

The substance, either solid or dissolved, becomes yellow in sunlight and remains in this form when left in darkness; the above solution in acetone, after six hours in sunlight, gave $[\alpha]_D 282^{\circ}$, whence $[M]_D 1365^{\circ}$, unchanged after twelve hours in darkness.

pp'-Bisiminocamphordiphenylamine (I or II).

Camphorquinone (1.66 grams), *pp'*-diaminodiphenylamine (1 gram), and fused sodium acetate were heated on the water-bath during two hours, the product being extracted with absolute alcohol, precipitated by water, and redissolved in hot alcohol, from which the substance crystallised (Found: $N = 8.06$. $C_{32}H_{37}O_2N_3$ requires $N = 8.48$ per cent.). It forms yellow prisms melting at $210-212^{\circ}$, and is insoluble in water, but dissolves in chloroform, benzene, or methyl alcohol, and less readily in ethyl alcohol. The alcoholic solution develops a greenish-red coloration with ferric chloride, and a deep, but transient, cherry red with mineral acids, becoming yellow with alkalis and returning with acids. It dyes wool yellow with alum, and somewhat deeper with chrome in an alcoholic bath of 2 per cent. The fluorescence in organic solvents is a feeble green, and there is no mutarotation:

Solvent.	Gr./100 c.c.	Temper- ature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.1300	23°	5.98°	2300°	11385°
" (brown form)...	0.0364	30	1.72	2370	11731
Methyl alcohol	0.0554	23	2.77	2500	12375
Acetone	0.0376	19	1.99	2646	13097
Ethyl alcohol	0.0440	"	2.53	2875	14231
Pyridine	0.1084	30	5.82	2685	13288

Exposure to sunlight during a few minutes converts the substance into a brown modification which does not revert in darkness, but becomes yellow when heated above 75° . The two forms and their

mixture melt at the same temperature and have the same rotatory power.

For comparison with aryl derivatives of bisiminocamphor the parent substance, azocamphanone, was examined in the polarimeter (compare Forster and Zimmerli, T., 1910, 97, 2165) :

Solvent.	Gr./100 c.c.	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
Chloroform	0.2605	30°	0.98°	188°	616°
Methyl alcohol	0.1660	„	0.76	229	750

Hydrochlorides of Bases in Condensation.

Free tolidine and dianisidine do not undergo condensation with camphorquinone even at high temperatures (120--125°) and with prolonged heating alone, or with sodium sulphate or zinc chloride. Action proceeds readily with the hydrochlorides, however, and benzidine combines in either form (compare G. M. Robinson and R. Robinson, T., 1918, 113, 644).

One of us (M. S.) desires to make acknowledgment to the Punjab University for the Macleod-Kapurthala Research Scholarship which has enabled him to collaborate.

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[Received, November 1st, 1921.]

CCXXVI.—*The Reversibility of the Michael Reaction.*

By CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL.

ALTHOUGH the condensation of $\alpha\beta$ -unsaturated esters with sodium derivatives of compounds of the type of ethyl malonate, generally known as the Michael reaction, is one of the most valuable methods of synthesis in the hands of the organic chemist, its mechanism and controlling conditions appear to have received singularly little attention. This is particularly remarkable when it is recalled that the mechanism of the acetoacetic ester condensation, of the Perkin reaction, and indeed of most of the important synthetical processes, has been the subject of protracted controversies.

During the course of an inquiry into the reason why certain attempts to produce derivatives of methanetriacetic acid by means of the Michael reaction met with no success, facts were discovered (Ingold and Perren, this vol., p. 1865) which strongly suggested that the Michael condensation is a reversible process, at least in the particular series of compounds dealt with. Therefore it seemed of

interest to ascertain (a) whether the reversibility of the reaction is a general phenomenon, (b) further, supposing this to be so, how the tendency towards reversion is conditioned by the structures of the substances concerned, and (c), finally, how the equilibrium, in any particular case, may be displaced in a desired direction by adjusting the experimental conditions. The present paper is a preliminary attempt to find the answers to these questions, which will now be discussed in turn.

(a) It is convenient to adopt the equation

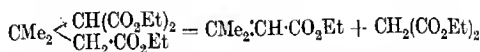


where U is an unsaturated ester, M the sodio-derivative of malonic ester or some other ester of a similar type, and C the condensation product, as a symbolic expression in general terms of any Michael condensation; the converse equation



will therefore denote any retrograde Michael condensation. Now it so happens that in all the instances previously recorded (*loc. cit.*) reaction (ii), when observed at all, proceeded so nearly to completion that it was impossible to obtain the condensation product *C* by the corresponding direct reaction (i). *C* had to be produced by an indirect means (introducing the substituted acetic acid chains in a different order) which, however, cannot be employed excepting in the methanetricetic acid series. Therefore, in order to establish the generality of the phenomenon, it was essential to select for examination instances (outside the methanetricetic acid series) in which there would appear to be a more even balance between the reactions (i) and (ii). On examining the literature, and, in particular, the yields of condensation products obtained by various investigators, it quickly became apparent that the vast majority of the recorded instances of condensations between ethyl malonate and esters of the acrylic acid series probably belong to this category, and it was decided, consequently, to approach the problem by reinvestigating two typical condensations which have some claim to be regarded as being amongst the most classical instances of the Michael reaction. The examples chosen were (α) the condensation of ethyl cinnamate with ethyl malonate, the first recorded instance of the reaction (Michael, *J. pr. Chem.*, 1887, [ii], 35, 351), and (β) the condensation of ethyl β-dimethylacrylate with ethyl malonate, a reaction which formed the starting-point of most of the earlier important synthetical experiments dealing with the constitution of camphor and its degradation products (Goodwin and Perkin, *P.*, 1894, 10, 64; *T.*, 1896, 69, 1472; Auwers, *Ber.*, 1895, 28, 1130; *Annalen*, 1896, 292, 145; Perkin and Thorpe, *T.*, 1899, 75, 51).

In the first place, it was necessary to show that the retrograde reaction could be realised in these instances. This presented no difficulty, for when the pure condensation products (ethyl β -phenylpropane- $\alpha\gamma$ -tricarboxylate and ethyl $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -tricarboxylate) were dissolved in alcoholic solutions containing equivalent quantities of sodium ethoxide, and heated at 100° under the conditions usually employed in carrying out ordinary Michael reactions, fission occurred to the extent of approximately 60 per cent. in the sense of the following equations :



From this result the attainment of equilibria appears to follow as a necessary corollary. Moreover, it rapidly became clear in the course of the experimental investigation that essentially *the same* equilibrium is invariably attained, no matter whether it be approached by the direct or by the retrograde process; no matter, therefore, whether the starting-point be the pure product *C*, or a mixture of equivalent amounts of the constituent esters *U* and *M*, or any mixture of this mixture with the ester *C*, always provided that sufficient time be allowed for the equilibrium to be reached.

(b) It would be a matter of the greatest interest to obtain a collection of accurate values for the equilibria with ethyl malonate at different temperatures and concentrations of a series of α - and β -substituted acrylic esters. Unfortunately, the method of separating by fractional distillation the three esters present at equilibrium is a cumbersome and inaccurate way of estimating their relative proportions, but for lack of suitable analytical processes this has been the method employed in the present investigation. However, where similar experimental conditions have been used, the yields obtained are in moderately close agreement with those recorded by previous workers (*loc. cit.* *Vide* also Michael, *Ber.*, 1900, **33**, 3748; Perkin, *T.*, 1896, **69**, '467), and the following table is probably a not very inaccurate statement of the equilibria which can be reached under the customary experimental conditions (Solvent: 99.8 per cent. ethyl alcohol. Concentration: 300 grams of alcohol for gram-molecular quantities of the reactants).

Condensation Product (<i>C</i>).	Yield of <i>C</i> (per cent.).	
	Temp. 100° .	Temp. 25° .
Ethyl β -methylpropane- $\alpha\gamma$ -tricarboxylate	65	?
" β -phenylpropane- $\alpha\gamma$ -tricarboxylate	35	70
" $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -tricarboxylate ...	30	50
" $\alpha\beta\beta$ -trimethylpropane- $\alpha\gamma$ -tricarboxylate ...	trace?	?

The effect on ring closure of the *gem*-dimethyl group, and in general of substituents of considerable atomic or molecular volume, has been emphasised in two recent communications (Ingold, this vol., pp. 305, 951). It has been proved, for instance, that derivatives of $\beta\beta$ -dimethylglutaric acid pass, by the interaction of substituents attached to the two acetic acid chains, into cyclic compounds more readily than do similar derivatives of glutaric acid. There is much evidence tending to show that the acetic acid residues are in closer proximity in the former case than in the latter. It seems, therefore, very reasonable to suppose, for instance, that the acetic and malonic ester chains in ethyl $\beta\beta$ -dimethylpropane- α -xy-tricarboxylate are in closer proximity than those in ethyl β -methylpropane- α -xy-tricarboxylate; further, because the accumulation of bulky groups in a restricted space is invariably a condition of instability, it must follow that the convergence of these chains caused by the groups attached to the β -carbon atom of the glutaric acid derivative must determine its tendency towards decomposition into smaller molecules. It is obvious from the table that this tendency towards disruption is greater in the case of the $\beta\beta$ -dimethyl compound than with the β -methyl analogue. The single phenyl group occupies a position intermediate between the single methyl group and the *gem*-dimethyl group, whilst the remarkable effect of introducing a substituent into the acetic acid chain, an effect so noticeable in the methanetriacetic acid series (*loc. cit.*), is again observed in the case of the trimethyl compound.*

We have, therefore, a method of considerable potential value for determining the effect of substitution on the stability of a carbon chain, but it is unfortunate that in this field, in which certain thermal and thermochemical determinations would be of the greatest service, very few measurements have been made. It would appear, however, that the heat of a reaction of type (i) is usually positive, and that, as follows from the formula $d \log_e K/dT = -QR^{-1}T^{-2}$, the equilibrium moves in the direction which favours the product *C* when the temperature is reduced. Moreover, the same formula shows that *Q* must be greater for the condensation between ethyl malonate and ethyl cinnamate than for that between ethyl malonate and ethyl dimethylacrylate, although no direct experimental

* The effect of the electrochemical character of substituent groups is also easily appreciable, as many instances, which lie without the scope of this paper, show. The larger yields of condensation products obtained when ethyl malonate is replaced by ethyl cyanoacetate (compare, for instance, Perkin and Thorpe, T., 1899, 75, 52) may be attributed in part to the more intense polar character of the CN-group, but here again the difference is in the sense which accords with the relation between the molecular volumes of the groups concerned.

determinations have as yet been made. As Nernst (*Wied. Annalen*, 1894, 53, 57), Böldlander (*Zeitsch. physikal. Chem.*, 1898, 27, 55), and others have shown, Q and the osmotic work A do not differ by much if no gaseous substances take part in the equilibrium, and it is the common value towards which Q and A converge which is the true measure of the stability of the molecule.

(c) The above considerations show that if it be desired to prepare the compound C by means of reaction (i), there are certain factors by adjusting which the equilibrium may be caused to move in the direction favouring the production of that substance. Thus the equilibrium may be disturbed by some further change, either physical or chemical. To take a single instance of the effect of concentration, if two-thirds of the theoretical quantity of ethyl cinnamate be used in the preparation of ethyl β -phenylpropane- $\alpha\gamma$ -tricarboxylate, the yield obtained on allowing the reaction to take place at 25° (other conditions being as indicated on p. 1973) is more than 80 per cent. of the theoretical, calculated on the ethyl cinnamate employed.

The table on p. 1978 shows in a very clear manner the effect of lower temperatures on the equilibrium quantities of the condensation products. It is curious that none of the investigators previously referred to, for whom the preparation of ethyl β -dimethylpropane- $\alpha\gamma$ -tricarboxylate was the starting-point of their synthetical experiments, appears to have tried the effect of lower temperatures with a view to improve the yields, which, under the conditions they employed, were always poor. Michael, on the other hand, was fully aware that better yields of ethyl β -phenylpropane- $\alpha\gamma$ -tricarboxylate could be obtained by conducting the reaction in the cold, but he did not appreciate the fact that the cause of this lay in the simultaneous occurrence of the retrograde process.

EXPERIMENTAL.

The general plan of these experiments, as well as the results obtained, has been fully described above, and only a few minor details need be added here, since the method of conducting Michael condensations is well known.

Identity and Purity Criteria.

The ethyl malonate and ethyl cinnamate employed were carefully purified by distillation, and the ethyl β -phenylpropane- $\alpha\gamma$ -tricarboxylate required for the experiments on the retrograde reaction was prepared from the other two esters by condensation at a low temperature. It was purified by distillation (b. p. 220–224°).

25 mm.), and its purity controlled by analysis (Found: C = 63.9; H = 7.3. Calc., C = 64.3; H = 7.1 per cent.).

The products of the retrograde reaction (type ii) were separated by fractional distillation. The ethyl cinnamate was identified by its boiling point (270–274°), by analysis (Found: C = 74.6; H = 6.9. Calc., C = 75.0; H = 6.8 per cent.), and by hydrolysis to cinnamic acid, and the ethyl malonate by its boiling point (195°) and by conversion into malonamide.

Ethyl dimethylacrylate was prepared from ethyl α -bromoiso-valerate and quinoline (Perkin, *loc. cit.*) and was so distilled as to remove the trace of volatile impurity that often causes the freshly-distilled ester to turn pink. The ethyl $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -tricarboxylate, prepared from ethyl dimethylacrylate and ethyl malonate by condensation at 35°, was purified by distillation (b. p. 181°/28 mm.), and its purity checked by analysis (Found: C = 58.4; H = 8.4. Calc., C = 58.3; H = 8.3 per cent.).

The ethyl dimethylacrylate isolated from the retrograde reaction (type ii) was identified by its boiling point (155°), by analysis (Found: C = 65.3; H = 9.3. Calc., C = 65.6; H = 9.4 per cent.), and by hydrolysis to dimethylacrylic acid. The ethyl malonate was identified as in the previous instance.

Times Required to Attain Equilibria.

Equilibrium is attained more rapidly between ethyl malonate, ethyl cinnamate, and ethyl β -phenylpropane- $\alpha\gamma$ -tricarboxylate than between ethyl malonate, ethyl $\beta\beta$ -dimethylacrylate, and ethyl $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -tricarboxylate. In the former case, heating for six hours at 100° or for one week at 25° suffices for the approximate attainment of the equilibria characteristic of these temperatures, whilst in the latter it is better to heat the mixture for about twenty-four hours at 100° or for two weeks at 35°.

Method of Conducting Retrograde Reactions (Type ii). Example: Decomposition of Ethyl β -Phenylpropane- $\alpha\gamma$ -tricarboxylate into Ethyl Cinnamate and Ethyl Malonate.

The following instance illustrates the method employed. Ethyl β -phenylpropane- $\alpha\gamma$ -tricarboxylate (100 grams) was added to a solution of sodium (6.8 grams) in absolute ethyl alcohol (89 grams), and the mixture heated at 110° in a closed vessel for seven hours. It was then cooled as quickly as possible, poured into dilute hydrochloric acid, and the esters isolated by extraction with ether in the usual manner. On distilling the product under diminished pressure, 30 grams (30 per cent.) of ethyl β -phenylpropane- $\alpha\gamma$ -tricarboxylate

were recovered (b. p. 220—224°/25 mm.), together with a more volatile fraction, which, on refractionating at the ordinary pressure, yielded 31 grams (60 per cent.) of ethyl cinnamate (b. p. 270—274°), and a quantity of ethyl malonate. Malonic acid also was recovered from the aqueous liquors. Ten per cent. of the material remained to be accounted for as experimental losses.

We gratefully acknowledge our indebtedness to Professor J. F. Thorpe for his interest in this investigation. Part of the cost was defrayed from a grant made by the Chemical Society, to whom also we wish to record our thanks.

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CCXXVII.—Complex Metallic Ammines. Part VI. cis-Phthalato-, cis-Homophthalato-, and other Di- ethylenediaminecobaltic Salts.

By JAMES COOPER DUFF.

IN Part V (this vol., p. 385), a number of cobaltamine salts were described, which were derived from six dibasic aliphatic acids and contained a seven-membered ring in the complex. Werner (*Annalen*, 1911, 386, 26, 81) was of the opinion that complexes containing a higher number of atoms to the ring than six could not be obtained. In Part V it was pointed out that Werner was using acids of a type unsuitable to the formation of a ring of more than six atoms in the complex.

The results obtained in Part V (*loc. cit.*) showed that the complex could be enlarged in molecular size, and it was therefore of interest to investigate what increase in size of the complex was possible. Price and Brazier (*T.*, 1915, 107, 1367) showed that an eight-membered ring was possible by introducing the sulphur atom into the ring, using for the purpose sulphonyldiacetic acid. It was decided to investigate the results obtained by using aromatic dibasic acids. In addition to the ring formation, the complex would be increased in molecular size by the benzene ring.

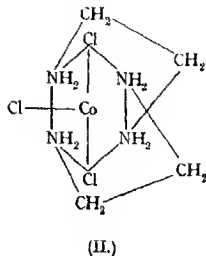
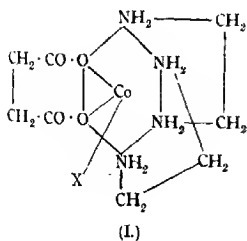
Phthalic acid was found to give crystalline compounds containing the phthalato-radicle in the complex. This means that the complex in these compounds contains a seven-membered ring and the benzene ring in addition. Phthalato-compounds, as is to be expected, are formed more readily than the corresponding succinato-

compounds (*loc. cit.*, p. 387), since phthalic acid gives an anhydride more readily than does succinic acid.

Price and Duff (T., 1920, 117, 1072) have described the introduction of the sulphaacetato-radicle into the complex. It has now been found possible to introduce the benzylsulphaacetato-radicle. *o*-Sulphobenzoic and bromobenzene-3:4-disulphonic acids have been used and both yield crystalline compounds which contain a seven-membered ring, and a benzene ring in addition. These results correspond with those obtained from sulphaacetic acid and methionine acid (Price and Duff, *loc. cit.*), but lead to one more carbon atom in the ring system.

Glutaric acid has been tried for the purpose of forming an eight-membered ring in the complex, but it has not produced any crystallisable compounds. Homophthalic acid has, however, given crystallisable compounds which represent the first compounds with a complex containing eight atoms in the ring, without the presence of sulphur.

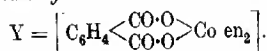
The compounds which have been obtained show that it is possible to increase the size of the complex considerably more than Werner considered possible. The results give support to the shell formula suggested by Friend (this vol., p. 1045), since the zone round the cobalt atom is not increased in size by these acids, as is the case with the co-ordination formula suggested by Werner. It should be noted that the formula, which Friend (*loc. cit.*) gives for succinato-diethylenediaminecobaltic salts, is not the most probable. Werner has shown that the corresponding carbonato- and oxalato- salts can be resolved into optically active isomerides. In the shell formula, cobalt cannot be considered asymmetric, and the optical activity is due to nitrogen being a member of two ring systems. This is shown by having the ethylenediamine molecules interlocking. This interlocking is rendered more probable by the more stable character of the compounds compared with those formed from ammonia. Formula I would then represent the succinato-salts.



The author is not prepared to support the conclusion of Friend (*loc. cit.*) that oxygen atoms from an acid like succinic or fumaric acid could take up *para*-positions in the shell formula. *Trans*- or *para*- salts of the tetrammine series change colour in solution from green to purple, and Werner has shown conclusively that they are then *cis*- or *ortho*- salts, and can only be reconverted to *trans*- or *para*- salts by excess of a strong mineral acid like hydrochloric or hydrobromic acid. The formula of *trans*-dichlorodiethylenediaminecobaltic chloride, expressed by the shell theory, would be best written as formula II, so that in both the *cis*- and *trans*- salts the ethylenediamine molecules are interlocking. The shell theory, as Friend (*loc. cit.*) points out, receives even stronger support from compounds like the carbonato-pentammine salts.

EXPERIMENTAL.

cis-Phthalatodiethylenediaminecobaltic Salts, YX, where



The *bromide*, $YBr \cdot 3H_2O$, separated in minute, purplish-red plates when a hot solution of 2.60 grams of phthalic acid was poured into a boiling solution of 5 grams of carbonatodiethylenediaminecobaltic bromide in 100 c.c. of water, and the mixed solution was concentrated to a small bulk on the water-bath, and left in the ice chest (Found: Co = 12.21; Br = 16.52; H_2O = 11.52).

$C_{12}H_{20}O_4N_4BrCo \cdot 3H_2O$
requires Co = 12.36; Br = 16.76; H_2O = 11.32 per cent.).

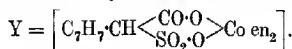
The phthalato-radicle was entirely in the complex, since no reaction could detect its presence until the bromide was well boiled with dilute hydrochloric acid, when phthalic acid could be crystallised out on cooling.

The *nitrate*, $YNO_3 \cdot 2\frac{1}{2}H_2O$, was obtained in fine, short, mauve needles by precipitating a solution of 3 grams of the bromide with 1.20 grams of silver nitrate, filtering and evaporating to small bulk (Found: Co = 12.99; N = 15.35; H_2O = 9.91. $C_{12}H_{20}O_4N_5Co \cdot 2\frac{1}{2}H_2O$ requires Co = 12.99; N = 15.43; H_2O = 9.91 per cent.).

The *hydrogen phthalate*, $Y \cdot CO_2 \cdot C_6H_4 \cdot CO_2H$, was obtained in microscopic, pink plates by adding 5.2 grams of phthalic acid to a boiling solution of the carbonato-base, prepared from 5 grams of the carbonato-bromide in 100 c.c. of water and 4 grams of freshly-prepared, moist silver oxide. The resulting solution was evaporated on the water-bath, and the salt separated in increasing quantity as the evaporation proceeded. It is almost insoluble in cold

water (Found: Co = 11.38; N = 11.01. $C_{20}H_{25}O_8N_4Co$ requires Co = 11.61; N = 11.03 per cent.).

cis-Benzylsulphoacetatodiethylenediaminecobaltic Salts, YX, where

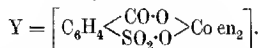


The *bromide*, $YBr \cdot 2H_2O$, was obtained in minute, red, flattened needles by adding 3.61 grams of benzylsulphoacetic acid in 50 c.c. of water to a hot solution of 5 grams of the carbonato-bromide in 100 c.c. of water, and then concentrating to low bulk and keeping for four weeks in the ice chest (Found: Co = 11.38; Br = 15.32; H_2O = 6.88. $C_{13}H_{24}O_5N_4BrSCo \cdot 2H_2O$ requires Co = 11.23; Br = 15.28; H_2O = 6.88 per cent.).

The *normal benzylsulphoacetate*, $Y \cdot CO_2 \cdot C_8H_8 \cdot SO_3 \cdot Y \cdot 4H_2O$, was obtained in the attempt to prepare the acid salt from two molecular proportions of the acid and one of the carbonato-base. After evaporation to low bulk and keeping for several weeks in the ice chest, the normal salt separated in microscopic, pink crystals (Found: Co = 10.58; N = 9.95; H_2O = 6.48.

$C_{35}H_{56}O_{15}N_8S_3Co_2 \cdot 4H_2O$
requires Co = 10.58; N = 10.05; H_2O = 6.46 per cent.).

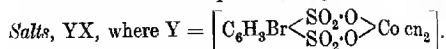
cis-o-Sulphobenzoatodiethylenediaminecobaltic Salts, YX, where



The *bromide*, $YBr \cdot H_2O$, was obtained in microscopic, purple-red crystals after the gradual addition of a solution of 3.27 grams of sulphobenzoic acid to a boiling solution of 5 grams of the carbonato-bromide in 100 c.c. of water, and evaporation to low bulk. Gradual addition of the acid was necessary to avoid the formation of the hydrogen sulphobenzoate, which was otherwise found to separate (Found: Co = 12.18; Br = 16.58; H_2O = 3.89.

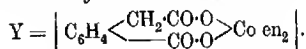
$C_{11}H_{20}O_5N_4BrSCo \cdot H_2O$
requires Co = 12.36; Br = 16.76; H_2O = 3.77 per cent.).

The *hydrogen sulphobenzoate*, $Y \cdot SO_3 \cdot C_6H_4 \cdot CO_2H$, was obtained in minute, pink plates from two molecular proportions of the acid and one of the carbonato-base in the usual way. It is much more soluble in water than the corresponding phthalato-hydrogen phthalate (Found: Co = 9.99; N = 9.55. $C_{13}H_{20}O_{10}N_4S_2Co$ requires Co = 10.16; N = 9.66 per cent.).

cis-Bromobenzene-3 : 4-disulphonatodiethylenediaminecobaltic

Bromobenzene-3 : 4-disulphonic acid was selected because it contains the two sulphonic acid groups in the *ortho*-position, and it was found to behave in a different manner from that of any of the other acids used (compare in this respect the results obtained with methionie acid, which is also a disulphonic acid; ¹T., 1920, 117, 1073). With the carbonato-bromide the acid produces the normal bromobenzene-3 : 4-disulphonate described below and hydrogen bromide is set free; the latter reacts with some of the carbonato-bromide to give the green *trans*-salt, $(\text{Br}_2\text{Co en}_2)\text{Br}$, which could be detected in crystalline form in the evaporated solution.

The bromobenzene-3 : 4-disulphonate, $\text{Y} \cdot \text{SO}_3 \cdot \text{C}_6\text{H}_4\text{Br} \cdot \text{SO}_3 \cdot \text{Y}$, was obtained in the usual way from three molecular proportions of the acid and two of the carbonato-base. When the two solutions were mixed, separation of the salt began almost at once, and more was obtained by evaporation at the room temperature in a vacuum desiccator over sulphuric acid. It was found that evaporating by heating caused the solution to turn brown, apparently through decomposition. The normal salt was obtained in pale pink, microscopic crystals (Found: Co = 8.93; N = 8.59; S = 14.56. $\text{C}_{26}\text{H}_{41}\text{O}_{18}\text{N}_8\text{Br}_3\text{S}_6\text{Co}_2$ requires Co = 9.05; N = 8.60; S = 14.74 per cent.).

cis-Homophthalatodiethylenediaminecobaltic Salts, YX, where

The bromide, YBr , was not obtained in a crystalline form, although a red powder answering to it in analysis and properties was obtained when ethyl alcohol was added to the very concentrated syrup obtained after evaporating a solution of 5 grams of the carbonato-bromide, to which 2.82 grams of homophthalic acid had been added. The powder obtained takes up moisture from the air unless it has been repeatedly washed with acetone and, finally, with ether. Although insoluble in ethyl alcohol, the powder is readily soluble in methyl alcohol.

The thiocyanate, $\text{Y} \cdot \text{SCN} \cdot \text{H}_2\text{O}$, was obtained from the foregoing product by adding 2 grams of ammonium thiocyanate to a strong solution of 2 grams of the bromide. The thiocyanate separates at first in a viscid condition, but after being well washed with water and redissolved in warm water, it can be crystallised in minute, purple,

irregular plates, after evaporation in a desiccator (Found: Co = 13.50; N = 15.93; H₂O = 4.28. C₁₄H₂₂O₄N₃SCo.H₂O requires Co = 13.61; N = 16.18; H₂O = 4.16 per cent.).

The *hydrogen homophthalate*, Y.CO₂.CH₂.C₆H₄.CO₂H, was obtained in pink, microscopic needles from two molecular proportions of the acid and one of the carbonato-base in the usual way, although addition of a few drops of alcohol after evaporation, and keeping for four weeks in the ice-chest were required to cause crystallisation. The salt was obtained in good yield. It is much more soluble in cold water than the corresponding product obtained from phthalic acid (Found: Co = 10.85; N = 10.51. C₂₂H₂₀O₈N₄Co requires Co = 11.00; N = 10.45 per cent.).

trans-Dichlorodiethylenediaminecobaltic Salts.

Price and Brazier (T., 1915, 107, 1713) have described a series of additive compounds formed from certain dibasic aliphatic acids and their acid salts of *trans*-dichlorodiethylenediaminecobalt. The five acids employed in the preparation of the *cis*-compounds described above have been used to discover their behaviour with *trans*-dichlorodiethylenediaminecobaltic chloride.

Benzylsulphoacetic acid, unlike malonic acid, does not give an additive compound. It agrees in its behaviour with sulphoacetic acid (T., 1920, 117, 1075).

trans-Dichlorodiethylenediaminecobaltic hydrogen benzylsulphoacetate, (Cl₂Co en₂)SO₃.C₈H₈.CO₂H, separated readily in grass-green needles when 2 grams of *trans*-dichlorodiethylenediaminecobaltic chloride were stirred into a solution of 2 grams of benzylsulphoacetic acid in 30 c.c. of water (Found: Co = 12.25; Cl = 14.55. C₁₃H₂₅O₅N₄Cl₂SCo requires Co = 12.31; Cl = 14.81 per cent.).

Phthalic acid, like succinic acid, does not form an additive compound. As phthalic acid is not sufficiently soluble in water, it was necessary to use sodium hydrogen phthalate. An alcoholic solution was tried unsuccessfully.

trans-Dichlorodiethylenediaminecobaltic hydrogen phthalate separated almost quantitatively in emerald-green plates when a solution of 5 grams of sodium hydrogen phthalate in 25 c.c. of water at 50° was poured into a cold solution of 4 grams of the *trans*-dichloro-chloride in 20 c.c. of water (Found: Co = 14.09; Cl = 16.81. C₁₂H₂₁O₄N₄Cl₂Co requires Co = 14.21; Cl = 16.63 per cent.).

Sulphobenzoic acid also does not give an additive compound.

trans-Dichlorodiethylenediaminecobaltic hydrogen sulphobenzoate, (Cl₂Co en₂)SO₃.C₆H₄.CO₂H, separated in dark green, elongated plates on adding 2 grams of the *trans*-dichloro-chloride to a solution

of 4 grams of sulphobenzoic acid in 25 c.c. of water and keeping for two hours (Found : Co = 13.00; Cl = 15.61. $C_{11}H_{21}O_6N_4Cl_2SCo$ requires Co = 13.08; Cl = 15.72 per cent.).

Homophthalic acid was tried, both as the free acid and as the acid sodium salt, with the *trans*-dichloro-chloride, but no crystals could be obtained either of an additive compound or of an acid homophthalate.

Bromobenzene-3 : 4-disulphonic acid behaves differently from all acids previously used, in its action on the *trans*-dichloro-chloride. When solutions of the two substances were mixed, instead of a green *trans*-dichloro-salt forming, all the chlorine was displaced by the organic acid and a *cis*-salt soon separated in microscopic, pink crystals. This was found to be the bromobenzene-3 : 4-disulphonatodiethylenediaminecobaltic bromobenzene-3 : 4-disulphonate already described (Found : Co = 9.10; N = 8.65. Calc., Co = 9.05; N = 8.60 per cent.).

Since the work of Price and Brazier (*loc. cit.*), no other acids have so far yielded additive compounds of the type they describe.

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[Received, October 11th, 1921.]

CCXXVIII.—*The Separation of Miscible Liquids by Distillation.*

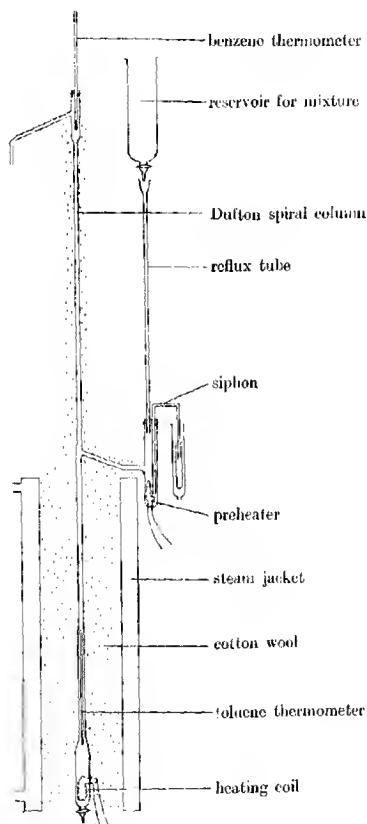
By ARTHUR FELIX DUFTON.

THE object of the present research is the investigation in the laboratory of continuous distillation. This involves the construction of continuous stills capable of effecting in the laboratory the perfect separation of a simple binary mixture such as benzene and toluene, which has hitherto not been achieved, and the study of their behaviour. A quantity, termed the thermal efficiency, has been defined by the author (*Phil. Mag.*, 1921, [vi], 42, 639) to afford a comparison of the performance of stills and a measure of the approach towards theoretical perfection.

A typical column for continuous distillation consists of a vertical tube into the middle of which the mixture to be distilled is introduced. The more volatile component is collected at the top of the column and the less volatile at the bottom. The upper part, that is, the portion above the point at which the mixture is intro-

duced, behaves exactly like a still-head for discontinuous working and must lose a certain amount of heat either throughout its length or to a condenser at the top. To the lower part of the column,

FIG. 1.



on the other hand, heat must be supplied either throughout the length or to a boiler at the bottom. When the whole of the heat is supplied at the bottom, loss of heat from the column must be reduced to a minimum.

As the only form of still-head capable of giving perfect separation in the laboratory appeared to be the column devised by Dr. S. F. Dufton (*J. Soc. Chem. Ind.*, 1919, **38**, 45r) for the separation of small quantities of liquids, it was decided to construct a continuous model upon the same principle. This type of column is made by creating a spiral track in a narrow annulus between a glass tube and an inner core upon which a spiral of wire is wound. Descending liquid seals the wire to the walls of the annulus and causes the ascending vapour to pass along the spiral track.

The first successful column made was 200 cm. long and the internal diameter increased from 0.45 cm. at the top to 0.9 cm. at the bottom (Fig. 1). Heat was supplied electrically at the bottom of the still by means of a wire coil immersed in the toluene and the rate of heating was measured by means of a watt-meter. To obviate any loss of heat from the lower half of the column, a thick lagging of cotton-wool was employed and this lagging was surrounded by a steam-jacket. As the temperature at the bottom of the still was 110° and at the middle of the still 90°, this protection was practically ideal. The upper half of the column was also lagged with cotton-wool.

The mixture to be separated was fed down a short reflux-tube into a small flask, where it was electrically preheated to its boiling point, and delivered into the middle of the column. A siphon maintained the level in the preheater constant and ensured a constant feed-pressure. The rate of feeding was regulated by altering the siphon level.

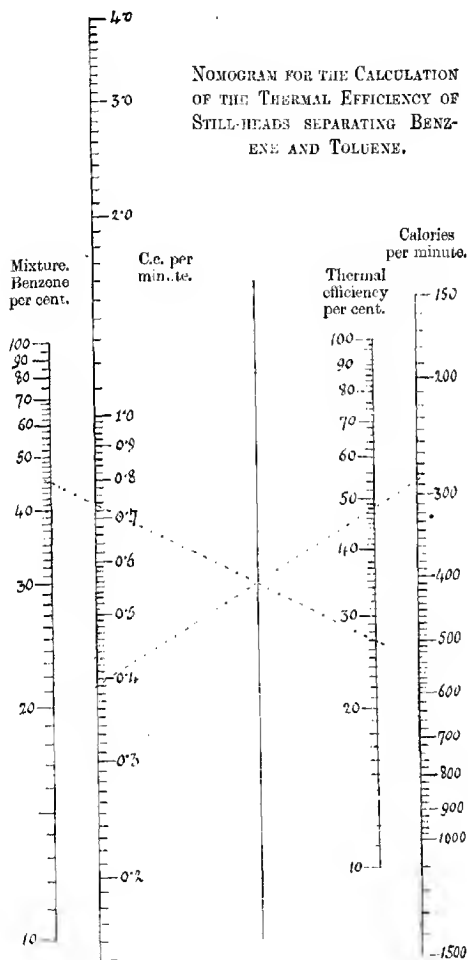
Thermometers reading to 0.1°, calibrated in position by the distillation of pure benzene and pure toluene, indicated the purity of the products. A small window was provided in the jacket to enable the boiling point on the toluene thermometer to be read. This thermometer formed the lowest portion of the core upon which the spiral track was wound.

The still could be regulated by altering the lagging upon the upper half, by adjusting the rate of feeding, and by varying the heat supply.

Tests were made with a 50 per cent. mixture of benzene and toluene, and it was found possible to regulate the still to work automatically, yielding pure benzene and pure toluene continuously, the temperatures indicated on the thermometers not differing by 0.05° from the calibrated temperatures. A rate of feeding of more than 0.5 c.c. per minute was attained.

In one experiment, with a heat supply of 309 calories per minute, pure benzene and pure toluene were collected each at the rate of 0.26 c.c. per minute. The separation of one gram of benzene required, therefore, the expenditure of 1340 calories. As the

FIG. 2.



theoretical quantity of heat required is calculated to be 208 calories (A. F. Dufton, *loc. cit.*) the thermal efficiency of the still was 15.5 per cent.

In another experiment with the same still, the lagging upon the upper half of the column was increased. With a rate of heating of 215 calories per minute pure benzene and pure toluene were collected each at the rate of 0.18 c.c. per minute. This also corresponds with a thermal efficiency of 15.5 per cent.

Further experiments with this type of column projected with a view to obtain an increased rate of feeding, a higher thermal efficiency, and easier regulation were discontinued, experiments, made concurrently with this investigation, having shown that

perfect separation in the laboratory is possible with other types of still-head. Some of the columns used appeared to be better adapted for continuous working than the Dufton column, which was specially designed to have minimum working volume, a matter of paramount importance in the separation of small quantities of liquid, but of no significance at all in continuous working.

FIG. 3.



In testing various still-heads, in a search for a simply constructed column giving with high thermal efficiency a pure product at a high rate of distillation per unit area of section and per unit volume of column, the mixture of benzene and toluene was boiled in a vacuum flask as still. Heat was supplied electrically by means of a coil of wire wound upon mica immersed in the liquid, and the rate of heating was measured by means of a watt-meter. The rate was controlled by means of a rheostat. A thermometer reading to 0.1° placed in the top of the column showed the temperature of the vapour and indicated the purity of the distillate. The thermometer was calibrated in position in the apparatus by the distillation of pure benzene, the boiling point, corrected for variation of atmospheric pressure, being

taken as 80.2° . The régime of distillation was so uniform that in one experiment a sudden change in the atmospheric pressure amounting only to 1.2 mm. was inferred from the reading of the thermometer before the reading of the barometer was made.

A nomogram (Fig. 2), constructed from data given in the author's paper in the *Philosophical Magazine*, was used to calculate the thermal efficiency from the rate of distillation, the rate of heating, and the composition of the mixture.

Tables I and II show the results obtained in experiments with a dephlegmator with 50 c.c. of 80 per cent. and 50 per cent. mixtures of benzene and toluene. A constant rate of heating of 287 calories per minute was maintained in each experiment.

The dephlegmator was made in a glass tube 1.5 cm. in diameter and the length of the column was 75 cm. To support the dephlegmating films of liquid, fifteen discs of copper gauze of 80 holes to the inch were sealed to the walls at intervals of 4.5 cm. A glass siphon tube 3 mm. in diameter was fitted through each disc (Fig. 3) to prevent the accumulation of liquid upon the gauze. These tubes acted as traps and prevented the vapour from ascending without bubbling through the liquid. The dephlegmator differed from that of Brown (T., 1880, 37, 49) in that the latter worked with a layer of liquid 8 mm. deep upon each gauze. Brown, moreover, used copper gauze of 40 mesh, stating that finer gauze would, "of course," mean greater pressure difference between sections. Experiment, however, shows the remarkable fact that the same pressure is required with gauze of 50, 60, or 80 mesh. The pressure required for a mixture of benzene and toluene was 2.5 cm. of liquid and the siphons were made to maintain this pressure.

TABLE I.

Time in minutes.	C.c. collected.	C.c. per min.	Benzene per cent. in the mixture.	Temp.	Thermal efficiency per cent.
0	0.0	—	80	—	—
6	3.3	0.60	79	80.2°	31
12	7.2	0.66	76.5	80.2	35
18	11.3	0.69	74	80.2	37
24	15.5	0.69	71	80.2	38
30	19.6	0.66	67	80.2	37
36	23.4	0.52	62.5	80.2	30
42	25.7	0.36	59	80.2	22
48	27.7	0.29	55	80.2	17
54	29.2	0.21	52	80.2	14
60	30.2	0.14	49.5	80.2	—
66	30.9	0.19	47.5	80.2	—

TABLE II.

Time in minutes.	C.c. collected.	C.c. per min.	Benzene per cent. in the mixture.	Temp.	Thermal efficiency per cent.
0	0.0	—	50	—	—
7.5	2.1	0.32	46	80.15°	22
15	4.8	0.39	45	80.2	27
22.5	7.9	0.40	41	80.2	29
30	10.7	0.35	36	80.2	27
37.5	13.1	0.30	32	80.2	25
45	15.2	0.22	28	80.2	21
52.5	16.3	0.15	26	80.2	15
60	17.3	0.10	24	80.2	13
67.5	17.8	0.06	22	80.2	—
75	18.2	0.05	—	80.2	—
82.5	18.6	0.03	—	80.2	—

Table III shows the results obtained with a still-head made by filling a glass tube 2.3 cm. in diameter and 100 cm. long with thin-walled, cylindrical, glass beads 4 mm. long and 4 mm. in diameter. A mixture of 500 c.c. of benzene with 300 c.c. of toluene was employed and the rate of heating was 1000 calories per minute throughout the experiment.

For a 50 per cent. mixture, the thermal efficiency was 47 per cent.; the rate of distillation was 0.60 c.c. per minute per sq. cm. of cross-section and 6.0 c.c. per minute per litre of still-head. This column is simple to construct, easy to operate, and not liable to become deranged. It appears to possess all the advantages sought for in a column for continuous working.

TABLE III.

Time in minutes.	C.c. collected.	C.c. per min.	Benzene per cent. in the mixture.	Temp.	Thermal efficiency per cent.
0	0	—	62.5	—	—
20	60	2.8	59.5	80.2°	47
40	113	2.7	57	80.2	47
60	165	2.6	53	80.2	47
80	219	2.5	48	80.2	47
100	271	2.4	43	80.2	47
120	314	2.05	38	80.2	45
140	353	1.7	33	80.2	40
160	382	1.4	28	80.2	38
180	408	1.1	23	80.2	33
200	423	0.8	20	80.2	27
220	438	0.7	17	80.2	27
240	451	0.6	14	80.2	27
260	462	0.4	11	80.2	24
280	468	0.3	10	80.2	17

The author desires to express his thanks to the Government Grant Committee of the Royal Society for funds placed at his disposal, which have defrayed part of the cost of this research.

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LONDON.

[Received, August 29th, 1921.]

CCXXIX.—*The Colour of Iron Alum.*

By JANE BONNELL and EDGAR PHILIP PERMAN.

It is well known to chemists that iron ammonium alum occurs in two distinct forms, namely, the more usual form of a violet colour and also a colourless form. Ostwald put forward the theory that

the latter is the pure form, the colour of the other being due to the presence of manganese as an impurity ("Grundlinien der anorganischen Chemie," 1900, 585). This might very easily be the case, and it was with the view of testing the validity of the hypothesis and of investigating the whole question that the following experiments were performed.

1. *Testing the Coloured Variety for Manganese.*—Some of the coloured variety was dissolved in water and the iron precipitated as basic acetate by means of ammonium acetate and acetic acid. This basic acetate was filtered off and thoroughly washed with warm water. The washings were added to the filtrate and the whole was evaporated to small bulk. Ammonium hydroxide was then added, the whole evaporated to dryness, and ignited. If manganese were present, it would be left as manganese oxide. Actually a faint black residue was left, which was tested for manganese by means of the borax bead test. The bead remained colourless both in the oxidising and the reducing flame, showing that the residue did not contain an appreciable quantity of manganese.

2. *Preparation of the Alum by Purifying from Manganese.*—This experiment was performed to test the previous result. Some of the coloured variety was dissolved in water and the iron partly precipitated as basic acetate. This basic acetate was filtered off and thoroughly washed as before. It was then dissolved in dilute sulphuric acid, and the solution divided into two portions, A and B.

A was converted into the alum. On crystallising, it gave coloured crystals.

In B, the iron was again partly precipitated as basic acetate, this basic acetate carefully washed as before, again dissolved in sulphuric acid, and then converted into the alum. This also yielded coloured crystals. It should be noted that both solutions A and B were strongly acid. Together, experiments 1 and 2 seem to show that the colour was not due to the presence of manganese, but was the colour of the pure salt.

3. *Preparation of Colourless Alum.*—These experiments fall into two divisions:

A. Attempts to prepare the colourless salt from the slightly reduced alum.

B. Attempts to prepare it from alum containing ferric hydroxide.

A. 1. A small quantity of the colourless alum was already available, as it had been prepared by a student in carrying out the preparation of iron alum as a practical exercise. On being tested, this was shown to contain ferrous salt, that is, there had been incomplete oxidation. A portion was oxidised with nitric acid in the presence

of sulphuric acid and allowed to crystallise. The solution yielded coloured crystals.

2. Some of the coloured alum was slightly reduced by means of sulphuric acid and iron filings. This solution yielded coloured crystals.

3. Some ferrous sulphate solution was added to a solution of the coloured alum and the whole allowed to crystallise. Coloured crystals were obtained.

Evidently, then, the loss of colour is not due to the presence of ferrous salts.

B. These experiments were based on the hypothesis that the colourless form might be due to the presence of ferric hydroxide.

1. A solution of the coloured alum was treated with a few drops of ammonium hydroxide and left to crystallise, when faintly brown crystals separated out.

2. Equal quantities of the crystals obtained in the previous experiment and of the violet crystals were dissolved together, and the solution was allowed to crystallise. The crystals obtained were still of a brown colour, but in both experiments the crystals showed no trace of the violet coloration of the original crystals.

3. A solution of the coloured alum in water was boiled for about ten minutes, and then allowed to crystallise, when colourless crystals separated out. It is known that solutions of this alum hydrolyse to an appreciable extent when heated, if strongly acid solutions are not used.

4. Some of the colourless crystals obtained were redissolved in water and the solution was made strongly acid. This yielded coloured crystals.

5. A saturated solution in cold water of the coloured alum was prepared and allowed to crystallise. The crystals did not separate out for about fifteen days and were of a mixed character, some being colourless and some having a faintly violet tinge. The colourless crystals were redissolved in cold acid solution and allowed to crystallise, when the violet crystals were obtained.

Conclusion.

These simple experiments point to the fact that the coloured form of the iron ammonium alum is the pure form of the salt. The colourless variety is due to the presence of ferric hydroxide (probably colloidal), the brown colour of which neutralises the colour of the alum itself. It has also been shown that simply boiling a solution of the alum for a few minutes, bringing about hydrolysis of the salt, produces sufficient ferric hydroxide to neutralise the colour, and to

make the solution yield colourless crystals, except when strongly acid solutions are used.

In ordinary circumstances, when the alum is being prepared, the solutions are strongly acid, very little hydrolysis takes place, and the coloured form is therefore produced.

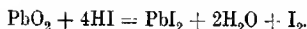
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CARDIFF.

[Received, October 19th, 1921.]

CCXXX.—The Direct Iodometric Estimation of Lead Peroxide.

By SAMUEL GLASSTONE.

THE method of the direct iodometric estimation of lead peroxide (or of red lead) without distillation was first introduced by Diehl (*Dingl. polyt. Journ.*, 1882, 246, 196). When lead peroxide is acted upon with dilute acid (acetic) in the presence of potassium iodide, the iodine liberated in accordance with the following equation may be directly titrated with standard thiosulphate solution.



An excess of ammonium acetate was added in order to keep the lead iodide in solution, as in the solid form it not only interfered with the detection of the end point, but also formed an insoluble coating round the solid peroxide and thus prevented further action. For this reason the acid used in the first place was acetic acid, as any stronger acid would be converted into it.

Topf (*Zeitsch. anal. Chem.*, 1887, 26, 277) slightly modified the method of Diehl, by using sodium acetate instead of ammonium acetate, and defined the quantities of the various reagents to be used in the estimation.

Reinsch (*Chem. Zentr.*, 1907, i, 993), Marchese (*Gazzetta*, 1907, 37, ii, 292), Beck (*Zeitsch. anal. Chem.*, 1907, 46, 456), and Milbauer (*Chem. Zeit.*, 1909, 33, 522) modified the Topf-Diehl method by varying the quantities of the substances used in the reaction.

Chwala and Colle (*Zeitsch. anal. Chem.*, 1911, 50, 209) examined the various modifications of this method and showed that uncertain results are caused by (a) the action of iodine on lead salts in the presence of acetic acid, resulting in the formation of methyl iodide, methyl acetate, and iodoacetic acid, and (b) the reversible reaction

$$6\text{H}^+ + 5\text{I}^- + \text{IO}_3^- \rightleftharpoons 3\text{I}_2 + 3\text{H}_2\text{O}$$

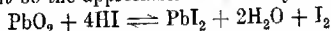
(Sammet, *Zeitsch. physikal. Chem.*, 35, 2)

1905, 53, 642), which prevents an appreciable amount of the iodine liberated by the lead peroxide from being titrated by thiosulphate.

Milbauer and Pivnicka (*Zeitsch. anal. Chem.*, 1914, 53, 345) made a fairly complete investigation of the various factors involved in the Topf-Diehl reaction, and obtained the following results: (a) the effect of time was to diminish the amount of "titratable" iodine formed, for example, when the results obtained were calculated as percentages of PbO_2 , the value obtained after ten minutes was 90.28, after twelve minutes, 89.6, and after sixty minutes, 86.0; (b) at higher temperatures (up to 60°) lower results were obtained, (c) 50 per cent. acetic acid gave a higher result than 5 per cent. acetic acid, (d) dilution to 200 c.c. gave higher results than dilution to 20 c.c., and (e) potassium and sodium acetates gave higher results than an equivalent amount of ammonium acetate. As a consequence of these investigations, the authors laid down conditions for the estimation of lead peroxide by this method; a glance at their experimental results, however, shows that the method cannot be regarded as by any means quantitative.

A further disadvantage of the Topf-Diehl method mentioned by Reinders and Hamburger (*Zeitsch. anorg. Chem.*, 1914, 89, 71) is the very slow rate of solution of the lead peroxide (or red lead) in the acetic acid mixture.

The object of this work was to find the conditions under which the interaction of lead peroxide and hydriodic acid would give quantitative and reproducible results. It seemed possible that a source of error, in addition to those given by Chwala and Colle (*loc. cit.*), might be the appreciable reversibility of the reaction,



(compare the similar reaction with hydrochloric acid, Wescott, *J. Amer. Chem. Soc.*, 1920, 42, 1335), and an experiment was arranged to test this possibility. If the conditions in the reaction are such that lead peroxide and lead iodide are solid phases, and the solution is moderately dilute, we should have, in the aqueous layer, $[\text{HI}]^4/[\text{I}_2]$ = a constant at a definite temperature.

EXPERIMENTAL.

A mixture of a large excess of lead peroxide and 20 c.c. of approximately *N*-hydrochloric acid containing 6 grams of potassium iodide was placed in a thermostat at 25° , and well shaken from time to time. After definite intervals, a known volume of the clear liquor was withdrawn, diluted, and rapidly titrated with *N*/10-thiosulphate, and then with *N*/10-sodium hydroxide.

Time.	C.c. of N/10. thiosulphate (a).	C.c. of N/10. NaOH (b).	2a + b.
30 mins.	8.1	3.0	19.2
60 "	9.4	0.4	19.2
180 "	9.6	nil	19.2
24 hours	9.6	nil	19.2

The results show that the reaction is not reversible to any appreciable extent, since all the hydrogen ions (as nearly as could be volumetrically determined) had been used up.

The uncertain results obtained in the Topf-Diehl method can be attributed only to the action of iodine on acetates and the formation of iodate (Chwala and Colle, *loc. cit.*). Both these sources of error would be eliminated by the use of hydrochloric acid instead of acetic acid, provided a means could be found of keeping the lead iodide in solution. The hydrogen-ion concentration would then be so great as to force the equilibrium in the iodate-iodide-iodine reaction well over to the free iodine side; for example, iodate may be estimated by adding acidified potassium iodide solution, and titrating the iodine quantitatively liberated. A further advantage in using hydrochloric acid would be the more rapid solution of the sample under analysis.

Solution of the Lead Iodide.

Sutton ("Volumetric Analysis," 10th ed., p. 138) and Schimpf ("Manual of Volumetric Analysis," 5th ed., p. 222) describe a method for estimating lead peroxide by digestion with hydrochloric acid and potassium iodide in a tightly stoppered bottle placed in a boiling-water bath. By this method the lead iodide is kept in solution during the course of the reaction (due to the elevated temperature), but the sparingly soluble salt separates out on cooling previous to titration. Milbauer and Pivnicka (*loc. cit.*) showed that a large excess of potassium iodide (40 grams for 0.2 gram of lead peroxide) kept the lead iodide in solution; this method is much too expensive.

The well-known solubility of lead haloids in solutions of alkali haloids led to the trial of sodium chloride; it was found that the presence of the latter salt greatly increased the solubility of lead iodide. Even in the presence of fairly concentrated hydrochloric acid, when the amount of sodium chloride in solution was greatly reduced, the solubility of the lead iodide was still considerable.

Concentration of the Acid.

The proposed method of estimation was to digest a weighed amount of lead peroxide (or red lead) with hydrochloric acid at room temperature in the presence of potassium iodide and a large

excess of sodium chloride. The effect of variation in the acid concentration on (a) the amount of iodine liberated, and (b) the rate of solution of the lead oxide and iodide, due to the corresponding alteration in the solubility of the sodium chloride, had to be determined. A series of experiments was arranged in which a definite weight of lead peroxide (0.2 gram) was added to 100 c.c. of hydrochloric acid varying in concentration from $N/2$ to $5N$, containing 1 gram of potassium iodide and excess (about 30 grams) of sodium chloride. The time for complete solution of the peroxide was roughly noted in each case and the iodine titrated against thiosulphate solution. The titrations were identical in each case, but when the hydrochloric acid was about $2N$, the rate of solution appeared to be greatest. This concentration, although not essential, was finally adopted for subsequent work. The amount of potassium iodide used in this process was always somewhat greater than that required by theory, owing to the sparing solubility of iodine in water. The iodide used must, of course, be free from iodate.

The effect of time on the amount of titratable iodine was also investigated; after three hours the titration was the same as that in a similar experiment in which the iodine had been titrated immediately.

In order to promote dissolution of the lead oxide, which in any case was far more rapid than in the Topf-Diehl method, the oxide was very finely ground, and the reaction carried out in a stoppered bottle which could be vigorously shaken. Under these conditions, no difficulty was ever experienced in getting specimens into solution.

These experiments showed that the direct iodometric estimation of lead peroxide could be put on a much better foundation than that of the Topf-Diehl method. The following procedure was then adopted for quantitatively estimating lead peroxide.

Method of Analysis.

Lead peroxide (0.2 gram) or red lead (0.5 gram) was weighed out into a bottle containing 20 c.c. of 36 per cent. hydrochloric acid, 100 c.c. of water, 20 to 25 grams of sodium chloride, and about 1 gram of potassium iodide. The bottle was stoppered and the whole well shaken for one or two minutes to ensure complete solution of the lead oxide. The liberated iodine was titrated with $N/20$ -thiosulphate solution, starch being added towards the end of the reaction. Very satisfactory duplicate results were obtained in this way. Owing to the uncertain results obtained by other methods of estimating lead peroxide (for a summary of these, see Chwala and Colle, *loc. cit.*), this method was checked by the estimation of lead in a pure lead salt (see below).

Small amounts of nitrate (a possible impurity in lead peroxide and in red lead) had no effect on the amount of iodine liberated.

The method described was also applied to the general estimation of lead, use being made of the oxidation of lead in boiling alkaline solution to lead peroxide by means of bromine water. A definite quantity of the lead salt was dissolved in water or in 5 per cent. sodium hydroxide solution; in either case alkali was added until the lead hydroxide had completely dissolved. Excess of bromine water was then added, and the mixture kept at or near the boiling point for some time (one to two hours) completely to convert the lead sesquioxide first formed into the peroxide, otherwise low results were obtained. The peroxide was then filtered off while hot and washed with boiling water (cold water gives colloidal filtrates) until free from bromine or hypobromite (test with acidified potassium iodide and starch). To ensure complete oxidation to peroxide, the precipitate may be digested with hot dilute acetic acid, and the filtrate made alkaline and again treated with bromine water. The filter-paper and contents were then placed in a bottle containing suitable quantities of hydrochloric acid, sodium chloride, and potassium iodide, for example, those recorded above. The bottle was well shaken to disintegrate the filter-paper, the contents were diluted with water and titrated with thiosulphate of suitable concentration. In this way results in agreement with the gravimetric estimation of lead as sulphate were obtained. This method is particularly useful in the case of very dilute solutions of lead salts where the gravimetric method is inapplicable; for example, 10 c.c. of a solution containing less than 0.004 gram of lead was easily analysed by this volumetric method.

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CCXXXI.—*The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part III. Products Derived from Halogenated Glutaconic Acids.*

By ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD.

It has been stated (this vol., p. 951) that the principal points in which Baeyer's Spannungstheorie is at variance with the known facts of organic chemistry fall into two classes, the first consisting

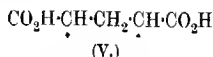
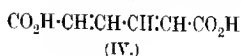
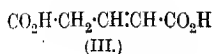
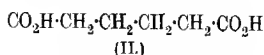
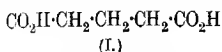
of those which relate to the effect on ring formation of the number of carbon atoms composing the ring, and the second those relating to the influence of substituent groups.

In the previous papers on this subject (this vol., pp. 305, 951) a series of definitely comparative experiments has been described by means of which, it is hoped, the precise extent of discrepancies of both types can be gauged with some degree of certainty. Such a series of experiments, if sufficiently extended, must in the end yield the information required for a restatement in more exact form of the fundamental conditions which underlie the formation and fission of carbon rings, and lead to a clearer comprehension of the reason for the fact that the tendencies to ring-formation and to fission are not strictly reciprocal properties; already, however, it has been noticed that many of the more obvious defects of the "Spannungstheorie," defects emerging, not only from *ad hoc* experiments, but also from a general survey of the literature of synthetic and naturally occurring carbocyclic compounds, disappear if the modifying hypothesis be made that groups attached to a carbon atom will, when not involved in ring formation, assume positions determined by their respective volumes relative to one another and to the available space.

The method employed in the experiments referred to, namely, measuring the extent to which ring formation occurs in competition with a uniform side reaction under standard experimental conditions, has been previously described (*loc. cit.*) in some detail, and, in view of the fact that the underlying hypothesis is capable of being expressed to a first approximation in a quantitative form, every effort has been and is being made to obtain all the accuracy of which the method is capable. In this way (compare Parts I and II) the formation of cyclopropane derivatives from *n*-propane compounds and of analogous cyclobutane derivatives from *n*-butane compounds has already been studied, and at the present time the investigation is being extended both to other types of ring and to rings containing substituents varying in number, position, and in kind. In the meantime, however, it seemed desirable to bring within the ambit of the investigation the study of a third influence regarding which very little precise information is at present available, namely, the influence of unsaturation on the formation of cyclic compounds.

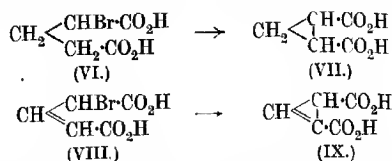
At the outset difficulty was experienced in selecting for investigation a suitable unsaturated acid capable of being treated according to the method used in the preceding parts of the research and at the same time having some claim to be regarded as a typical substance; for an examination of such information as exists indicated that totally different effects would be observed when dealing with

unsaturated compounds having differently situated double bonds. Since, however, in Parts I and II (*loc. cit.*) the open-chain substances employed were glutaric and adipic acids (I and II), it was ultimately decided to examine in a similar manner and under comparable conditions the corresponding unsaturated derivatives, namely, glutaconic and muconic acids (III and IV), although there can be no question but that neither of these acids can be regarded as a normal unsaturated substance.



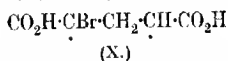
It is unnecessary to refer, except in the briefest manner, to the extended researches of Thorpe and his collaborators into the chemistry of the glutaconic acids. The clear outcome of this investigation has been that glutaconic acid is no ordinary unsaturated acid, and that, whilst it still possesses, although in greatly diminished degree, the characteristics of an unsaturated compound of the formula III, it has, in addition, another series of properties which this formula does not express and which suggest both symmetry of constitution and a condition of 1 : 3-unsaturation. The explanation offered is that the stable form of glutaconic acid has the "semi-aromatic" formula (V) (the "free" 1 : 3-valencies being associated sufficiently to limit to some extent the tendency towards 1 : 3-addition), but that in most experiments with the acid the unsaturated form (III) is present in small amount in a condition of tautomeric equilibrium. Many facts support this hypothesis. Nevertheless, it cannot be denied that in adopting such a formula for glutaconic acid one tacitly accepts the view that the chemistry of this substance consists largely of phenomena to which the ordinary three-dimensional formulæ-models can give no clue, and from this point of view the behaviour of glutaconic acid and its derivatives in relation to the requirements of the "Spannungstheorie" (which depends essentially on the tetrahedral carbon model) appears to possess more than ordinary interest.

Comparing, for instance, the formation of cyclopropane-1 : 2-dicarboxylic acid (VII) from α -bromoglutaric acid (VI) with the formation of Δ^2 -cyclopropene-1 : 2-dicarboxylic acid (IX) from α -bromoglutaconic acid (VIII) by the elimination of hydrogen bromide in each case, one observes that the unsaturated cyclic acid should be



considerably the more difficult to produce, the formation numbers (*loc. cit.*) in these instances being 0.345 and 0.385 respectively. Another factor, however, must be taken into account; for in all experiments of this kind it is essential to have some guarantee that the effects attributed to differing tendencies towards ring closure are not being masked by the differing reactivities of the halogen compounds employed. Indeed this consideration constitutes the main reason for employing the standard side-reaction method, since by this means any serious difference in the reactivities of the halogen compounds is immediately detected, and, in fact, is largely (although, in all probability, not exactly) compensated. The case with which we are here dealing furnishes the first instance so far met with in the course of these investigations of a halogen compound differing in reactivity from the analogues previously employed. The point of importance, however, is that the difference in this case is in the sense which again indicates that greater difficulty will attend the formation of the unsaturated ring acid (IX) than of the saturated acid (VII).

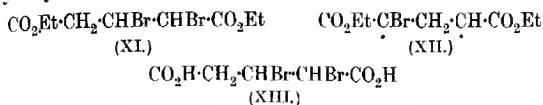
On two counts, therefore, the *cyclopropenedicarboxylic acid* should be less easily produced, but it will be a matter for surprise to no one prepared to regard α -bromoglutaconic acid as a "semi-aromatic" substance (X) having 1:3-valencies in an equilibrium



state of limited mutual association that, as a matter of fact, the *cyclopropenedicarboxylic acid* is produced considerably more smoothly than its saturated analogue under experimental conditions involving minimal complications in each case.

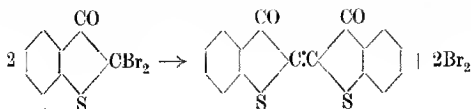
It is necessary at this stage, in order to render intelligible the significance of some of the factors which complicated the series of reactions from the products of which the *cyclopropenedicarboxylic acid* was isolated, to indicate the method by which the bromo-acid (X), or rather one of its esters, was obtained for the investigation. As Feist has shown (*Ber.*, 1911, 44, 135), ethyl glutaconate readily absorbs two atoms of bromine and yields a dibromo-ester (XI). This substance, when treated with diethylaniline under the conditions described in the experimental part of this paper, yields ethyl

bromoglutaconate (XII), in which the position of the bromine atom is clearly proved by the nature of the products formed on complete hydrolysis. The free dibromo-acid (XIII) was prepared by

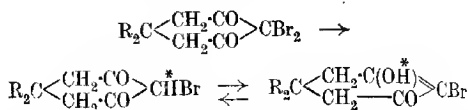


Verkade and Coups (*Rec. trav. chim.*, 1920, **39**, 586) by the action of bromine vapour on glutaconic acid in the absence of a solvent, but on attempting to prepare α -bromoglutaconic acid from this substance by elimination of hydrogen bromide, unexpected difficulties were experienced. Many experiments were made with a view to discover the correct conditions, but although indications were obtained that the monobromo-acid (X) was actually produced in considerable amount, it always appeared to be accompanied either by unchanged dibromide or by products of further decomposition, which, owing to the labile character of the bromine in the monobromo-acid, rendered purification exceedingly difficult. Since, therefore, after repeated attempts a satisfactory specimen was not obtained, the complete hydrolysis by alkalis of the dibromo-acid (XIII) was investigated under the usual two sets of standard experimental conditions in the hope that the character of the products would indicate the intermediate formation of the bromo-acid which it had not been possible to purify. This assumption proved in the main to be correct.

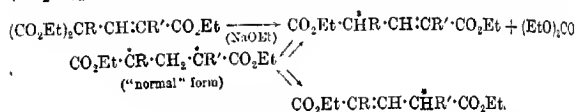
Nevertheless, when the dibromide was hydrolysed, certain reactions were observed which were not met with when the monobromo-ester was employed. Probably the most remarkable of these was that by which, under the influence either of concentrated or of dilute alkali, glutaconic acid (V) was produced with the elimination, not of hydrogen bromide, but of bromine, a type of reaction to which comparatively few parallels are known. However, those instances which have been recorded of the elimination of a halogen as such, either spontaneously or by some reagent (other than a reducing agent), are certainly to be regarded as indicating an exceedingly strong tendency towards formation of the product obtained. Thioindigotin, for example, is produced by merely heating 1:1-dibromo-2-ketodihydrothionaphthen (Bezdzik, Friedländer, and Koeniger, *Ber.*, 1908, **41**, 234), whilst several cases of the passage



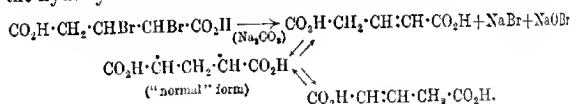
of the dibromo-derivative of a dihydroresorcinol into the corresponding monobromo-compound by the action of aqueous alkalis alone have quite recently been investigated (Norris and Thorpe, this vol., p. 1209-1210):



In the latter case, the great ease of formation of the product is almost certainly to be connected with the well-known tendency to acquire the mobile hydrogen atom (marked *) possessed by a potentially tautomeric system, a tendency well illustrated by the remarkable facility with which a carbethoxyl group is eliminated as ethyl carbonate from substituted glutaconic esters of the type $(\text{CO}_2\text{Et})_2\text{CR}\cdot\text{CH}\cdot\text{CR}'\cdot\text{CO}_2\text{Et}$ by the action of cold sodium ethoxide:



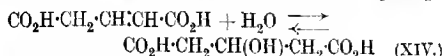
Once the mobile hydrogen atom (marked *) is obtained, the system becomes tautomeric and shows no further tendency to break down until interchange with the "normal" (semi-aromatic) form is again suppressed by replacing the hydrogen atom by an alkyl group (Thole and Thorpe, T., 1911, 99, 2187). The formal similarity with the hydrolytic reaction mentioned above is obvious:



Now the whole difference between the stability of three-carbon systems and that of tautomeric systems of other types is one of symmetry (Ingold and Thorpe, this vol., p. 492), the permanence of the "normal" form being dependent on this more than on any other separate factor. The normal form of glutaconic acid itself, therefore, is at once the most mobile in its dynamic and the most stable in its equilibrium relations with its unsaturated isomeride, of any normal acid of the series; hence it seems plain that the effect of molecular symmetry on three-carbon tautomerism is the ultimate cause to which the remarkable tendency towards the production of glutaconic acid, even by abnormal reactions such as the elimination of bromine from $\alpha\beta$ -dibromoglutaric acid and of nitrogen from esters

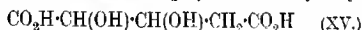
of pyrazole-3:5-dicarboxylic acid (compare p. 2009), is to be attributed.

The glutaconic acid obtained in these experiments was invariably accompanied by β -hydroxyglutaric acid (XIV), which was evidently a secondary product formed by the addition of the elements of water to the unsaturated form of glutaconic acid (III) during the process of isolation. Verkade has shown (*K. Akad. Wetensch. Amsterdam*, 1915, **18**, 981) that glutaconic acid unites with water in this manner when an acid solution is evaporated, whilst Fichter and Dreyfus (*Ber.*, 1900, **33**, 1452) proved that the reverse reaction proceeds in the presence of alkalis; hence the change is probably

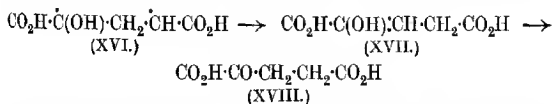


to be regarded as reversible, the equilibrium depending on the extent to which the end-products undergo further change under the conditions employed. Our observations on the matter appear to indicate that the principal circumstance affecting the equilibrium is the conversion in acid solution of the hydroxy-acid into a β -lactone or a lactide, which, however, is unstable and difficult to isolate.

Another acid the formation of which was observed in experiments on the action of alkalis on $\alpha\beta$ -dibromoglutaric acid was $\alpha\beta$ -dihydroxyglutaric acid, the product of complete hydroxylation* (XV). As with most hydroxylation products formed by similar methods, the quantity obtained (*vide* Tables I and II, p. 2011) was particularly large when dilute alkalis were employed for the hydrolysis.

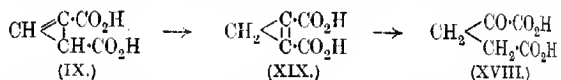


Regarding the substances obtained from ethyl monobromoglutaconate or from the monobromo-acid formed intermediately in the hydrolysis of $\alpha\beta$ -dibromoglutaric acid, it will immediately be obvious that the final hydroxylation product to be expected is α -ketoglutaric acid (XVIII), into which α -hydroxyglutaconic acid (XVI) must be converted (*via* its unsaturated modification, XVII) almost at the moment of its formation:



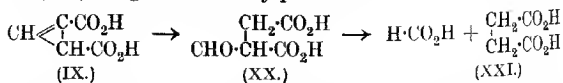
* Kiliani and Loeffler (*Ber.*, 1905, **38**, 3624) obtained this substance in small yield both by the action of permanganate on glutaconic acid and by boiling the acid in an aqueous solution to which the theoretical amount of bromine (two atoms) had been added. The latter observation is of interest, because $\alpha\beta$ -dibromoglutaric acid has never been obtained from the product formed by the action of bromine on glutaconic acid in the presence of water, or, indeed, of any other solvent (Thorpe, T., 1919, **115**, 679).

Actually, this keto-acid invariably constituted a considerable proportion of the product obtained whether concentrated or dilute alkalis were employed in the hydrolysis. This relatively slight difference, well illustrated by the figures recorded in Tables I and III (pp. 2011, 2012), between the quantities produced under the two sets of standard experimental conditions (one involving the use of 2*N*-aqueous sodium carbonate, the other of 6*N*-methyl alcoholic potassium hydroxide) which have been employed throughout this as well as in the preceding parts of the investigation, appeared the more unaccountable when considered in relation to the large differences obtained in other cases (*loc. cit.*), until it was suspected that α -ketoglutaric acid was the ultimate product of two distinct series of reactions. That this was really the case was satisfactorily proved by direct experiment; for it was found that the *cyclopropenedicarboxylic acid* (IX), although quite stable to dilute aqueous sodium carbonate, was decomposed somewhat readily by concentrated methyl-alcoholic potassium hydroxide forming amongst other products a considerable proportion of α -ketoglutaric acid. The reaction probably involves the transposition of the cyclic double bond followed by ring fission, and may be formulated as follows :



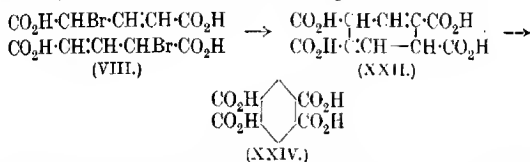
Plainly, therefore, whilst the whole quantity of the keto-acid obtained from the products of the hydrolyses by sodium carbonate is to be regarded as representing the extent to which hydroxylation occurred in these instances, the same inference cannot be drawn in connexion with the experiments in which methyl-alcoholic potassium hydroxide was employed, since a considerable proportion of the ketoglutaric acid produced in these cases must have been formed by the fission of the *cyclopropene* derivative (XIX).

A second substance formed by the hydrolytic decomposition of the *cyclopropenedicarboxylic acid* (IX) was succinic acid (XXI), which was always present in small amount in the products obtained when methyl-alcoholic potassium hydroxide was used. Obviously this acid must be formed by the fission of the *cyclopropenedicarboxylic acid* *without* previous migration of the double bond, acetic acid (XX) being intermediately produced :

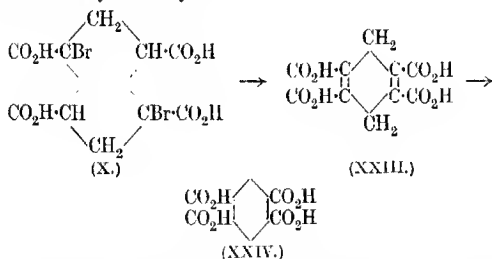


It is necessary now to refer to a reaction of a totally distinct type, a reaction, moreover, which appears to constitute a notable

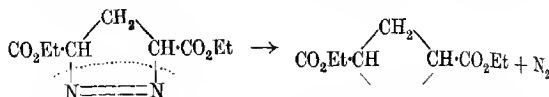
addition to the evidence already adduced that the abnormalities which characterise the transformations described in this paper are to be traced to the "semi-aromatic" character of the glutaconic acid derivatives employed. The final product of the change referred to is pyromellitic acid (XXIV), which has previously been obtained by Feist (*Ber.*, 1911, **44**, 135) from ethyl $\alpha\beta$ -dibromoglutarate, and in our experiments sometimes formed as much as 30 per cent. of the identified material (Tables I and III, pp. 2011, 2012). Now there is, of course, no difficulty in formulating the production of the dihydro-derivative (XXII) of pyromellitic acid (which obviously must be regarded as the primary product) from two molecules of the unsaturated modification of α -bromoglutaconic acid :



There are, however, many difficulties attending this interpretation. It is not clear, for instance, why not even a trace of pyromellitic acid is formed when $\alpha\gamma$ -dibromoglutaric acid is treated with alkalis under similar experimental conditions. If, however, the conception of limited 1 : 3-unsaturation, well grounded, as we believe, in the cases of glutaconic and β -methylglutaconic acids (Ingold and Thorpe, *loc. cit.*; Thorpe, *loc. cit.*), be extended to the α -bromo-derivative, then the formation of the aromatic acid appears to follow as an almost necessary corollary :

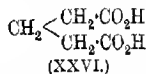
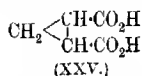


It may be remarked that this instance of the entrance of a "semi-aromatic" glutaconic acid derivative into the production of a larger ring is in some respects the counterpart of the formation of glutaconic ester (along with cyclopropane derivatives) by the elimination of nitrogen from ethyl pyrazole-3 : 5-dicarboxylate (Büchner, *Ber.*, 1890, **23**, 703; *Annalen*, 1893, **273**, 238) :

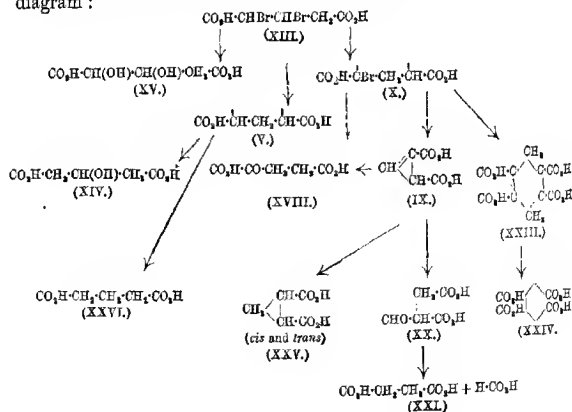


and that together these reactions indicate the degree of stability of the condition of partial association in which the "free" valencies of glutaconic acid are involved.

Finally, it is necessary to trace the history of the two atoms of hydrogen eliminated from the dihydropyromellitic acid (XXIII), and a reference to the tables (pp. 2011, 2012) will make it apparent that they are accounted for, at any rate largely, by the formation of reduction products, namely the *cis*- and *trans*-forms of cyclopropane-1:2-dicarboxylic acid (XXV) and glutaric acid (XXVI). One or both modifications of the former, evidently arising by reduction of the cyclopropenedicarboxylic acid (IX), were obtained from the products of all experiments in which the cyclopropenedicarboxylic acid itself was isolated. Glutaric acid, on the other hand, was obtained only in small amount in those experiments in which $\alpha\beta$ -dibromoglutaric acid was employed and in which, therefore, glutaconic acid was one of the substances formed.



The relationships between the various substances obtained by alkaline hydrolysis of $\alpha\beta$ -dibromoglutaric acid and α -bromoglutaconic acid (or ester) are summarised for convenience in the following diagram:



With regard to the quantitative aspect of the investigation, it must at once be admitted that owing to difficulties of separation scarcely more than 60 per cent. at most of the material employed was accounted for as pure products in any single experiment, and that for this reason the numbers obtained cannot be considered as numerically accurate expressions of the facts. Regarded broadly, however, they certainly do admit of some important generalisations. The quantities of the various products isolated were as follows :—

TABLE I.

	<i>αβ</i> -Dibromoglutaric acid (XIII).		Ethyl <i>α</i> -bromoglutarate (XII).	
	Dilute alk. (2 <i>N.</i> -aq. Na ₂ CO ₃).	Conc. alk. (6 <i>N.</i> -KOH in MeOH).	Dilute alk. (2 <i>N.</i> -aq. Na ₂ CO ₃).	Conc. alk. (6 <i>N.</i> -KOH in MeOH).
<i>αβ</i> -Dihydroxyglutaric acid (XV)	26	4		
Glutaconic acid (V)	2	5		
<i>β</i> -Hydroxyglutaric acid (XIV)	4	7		
Glutaric acid (XXVI) ...	trace (?)	2		
<i>α</i> -Ketoglutaric acid (XVII)	20	14	36	20
<i>cyclo</i> Propanedicarboxylic acid (IX)	4	2	6	3
<i>trans-cyclo</i> Propanedicarboxylic acid (XXV) ...	2	6	5	9
<i>cis-cyclo</i> Propanedicarboxylic acid (XXV) ...	0	1	0	4
Succinic acid (XXI) ...	0	2	0	5
Pyromellitic acid (XXIV)	3	10	7	17
Total isolated and identified	61	53	54	58%

From these figures it will be seen that, so far as can be judged from the amounts of identified material, the three simultaneous modes of decomposition of *αβ*-dibromoglutaric acid occur, under the two standard sets of experimental conditions, to the extents indicated in Table II, from which it is apparent that the formation of glutaconic acid is favoured by the use of concentrated alkalis, whilst the production of the hydroxy-acid takes place, as is usual, most smoothly under conditions of considerable dilution.

TABLE II.

	<i>αβ</i> -Dibromoglutaric acid (XIII).	
	Dilute alk.	Conc. alk.
<i>αβ</i> -Dihydroxyglutaric acid	43	9
Glutaconic acid and substances derived from it	10	25
Substances derived from <i>α</i> -bromoglutaric acid	57	66
	per cent. of identified material.	

Finally, we may group the substances derived from α -bromo-glutaconic acid or its ester into three heads according to the primary decompositions, hydroxylation, *cyclopropene*-ring-formation, *cyclo*-hexadiene-ring-formation, from which they are derived, obtaining in this way Table III; in reading which it must be remembered that for reasons explained on p. 2008 an unknown fraction of the whole quantity of α -ketoglutaric acid obtained from experiments in which concentrated alkali was used is to be attributed to the decomposition of the *cyclopropenedicarboxylic* acid (IX), and that, since α -keto-glutaric acid is also the hydroxylation product of α -bromoglutaconic acid, the figures entered represent only an upper limit to the degree in which this type of decomposition occurs, whilst, similarly, the figures given for *cyclopropene* ring-formation denote merely a lower limit to the extent of its actual occurrence.

TABLE III.

	α -Bromoglutaconic acid.		α -Bromoglutaconic ester.	
	Dilute alk.	Conc. alk.	Dilute alk.	Conc. alk.
α -Ketoglutaric acid	69	40	67	34
<i>cyclo</i> Propenedicarboxylic acid and products (other than α -ketoglutaric acid) derived from it	21	32	20	37
Pyromellitic acid	10	23	13	29
per cent. of identified material.				

The similarity between the figures referring to α -bromoglutaconic acid and its ester is rendered very obvious in Table III, and furnishes both a justification of the method adopted in studying the reactions of the bromo-acid, and a basis for the conclusion that the carboxyl groups probably play no very essential part in the series of changes observed. The figures which are not subject to the corrections mentioned in the preceding paragraph (that is, those in the first and third columns) are in particularly close agreement and by contrast with the results obtained in Part I (*loc. cit.*) constitute the grounds for the suggestion made on pp. 2003 and 2009 that the formation both of the three-carbon and six-carbon rings is in this instance to be attributed to a condition of limited 1 : 3-unsaturation pre-existing in the open-chain substances employed.

The investigation of the products derived from muconic acid is not yet complete and it is proposed to reserve the description of these for a future communication.

EXPERIMENTAL.

(A) *Halogen Derivatives of Glutaconic Acid.*

The $\alpha\beta$ -dibromoglutaric acid required for this investigation was prepared from glutaconic acid by Verkade's bromine-vapour method (*loc. cit.*) and was purified by crystallisation from anhydrous formic acid. Experiments made with the object of obtaining from it α -bromoglutaconic acid by elimination of hydrogen bromide were attended only with a limited degree of success, and ultimately the dibromoglutaric acid itself was subjected to complete hydrolysis by alkalis as described in sections B and C.

The ethyl $\alpha\beta$ -dibromoglutarate required for the preparation of ethyl α -bromoglutaconate (below) was obtained from ethyl glutaconate as described by Feist (*loc. cit.*).

Ethyl α -Bromoglutaconate (XII).

Slightly more than the theoretical quantity of diethylaniline was heated nearly to the boiling point and then quickly mixed with ethyl dibromoglutarate. If the materials were quite pure and the operation successful, the product was almost colourless and the neutral oil obtained from it by washing with dilute hydrochloric acid yielded on distillation almost the theoretical amount of ethyl α -bromoglutaconate, a colourless oil, b. p. 140--143°/10 mm. (Found: C = 40.6; H = 4.9; Br = 30.0. $C_9H_{13}O_4Br$ requires C = 40.7; H = 4.9; Br = 30.2 per cent.).

The action of dilute and of concentrated alkalis on this substance is described in sections D and E.

(B) *Action of Dilute Alkalis on $\alpha\beta$ -Dibromoglutaric Acid: Formation of $\alpha\beta$ -Dihydroxyglutaric Acid, Glutaconic Acid, β -Hydroxyglutaric Acid, α -Ketoglutaric Acid, Δ^2 -cycloPropene-1:2-dicarboxylic Acid, trans-cycloPropane-1:2-dicarboxylic Acid, and Pyromellitic Acid.*

Fifty grams of $\alpha\beta$ -dibromoglutaric acid (section A) were boiled with 500 c.c. of 2*N*-aqueous sodium carbonate for one and a half hours. The solution was then acidified by hydrochloric acid, evaporated to a thin paste, and extracted exhaustively with ether. When no more material could be recovered in this way, the pasty residue was dried and ground under cold acetone until only inorganic salts remained undissolved.

Pyromellitic Acid (XXIV).

The pale straw-coloured syrup obtained from the ether extract deposited crystals of pyromellitic acid hydrate on rubbing with water. The acid was identified by its melting point (242° for the dihydrate, 273° for the anhydrous acid), by analysis (Found: C = 47.2; H = 2.3. Calc., C = 47.2; H = 2.3 per cent.), and by the melting points of its methyl and ethyl esters (141° and 53° respectively). Methyl pyromellitate was also isolated from the less volatile fractions of the mixture of esters prepared as described on p. 2019.

 α -Ketoglutaric Acid (XVIII).

This acid may be isolated from the syrupy mixture either as its semicarbazone or phenylhydrazone, but the latter derivative was found to be more suitable for the purpose. It was obtained in the usual manner by means of phenylhydrazine acetate and hydrolysed to α -ketoglutaric acid by means of 30 per cent. sulphuric acid. The product extracted by ether from the acid solution melted at 110 – 112° , and after crystallising from a mixture of acetone and benzene, at 113° . It was identified as α -ketoglutaric acid by analysis (Found: C = 41.3; H = 4.1. Calc., C = 41.1; H = 4.1 per cent.), by the colour developed with aqueous-alcoholic ferric chloride, and by a mixed-melting-point determination with a genuine specimen (this vol., p. 328).

 $\alpha\beta$ -Dihydroxyglutaric Acid (XV).

The residue which remained when the acetone extract was evaporated consisted very largely of $\alpha\beta$ -dihydroxyglutaric acid, a considerable quantity of which crystallised on adding dry ether containing a trace of acetone. The acid melted at 164° and agreed in its properties closely with the description given by Kiliani and Loeffler (*loc. cit.*).

The syrupy mixture of acids recovered from the aqueous solution from which the phenylhydrazone of α -ketoglutaric acid was precipitated yielded a further quantity of $\alpha\beta$ -dihydroxyglutaric acid on mixing with successive quantities of dry ether. It was crystallised for analysis from a mixture of methyl acetate and dry ether (Found: C = 36.7; H = 5.1. Calc., C = 36.6; H = 4.9 per cent.).

 β -Hydroxyglutaric Acid (XIV).

The combined ethereal filtrates from the dihydroxyglutaric acid were evaporated, and the residue digested for several hours with

aqueous cupric acetate. The precipitate obtained in this manner was collected, decomposed by aqueous hydrogen sulphide, and the filtrate from the copper sulphide evaporated to dryness. The crystalline residue was finely powdered, exposed in an evacuated desiccator for several days, and then triturated with dry ether, which easily dissolved about half of it, leaving an insoluble portion consisting of a mixture of $\alpha\beta$ -dihydroxyglutaric acid and β -hydroxyglutaric acid. These acids were readily separated by crystallising from a mixture of ether and methyl acetate, and the β -hydroxyglutaric acid was identified by analysis (Found: C = 40.7; H = 5.3. Calc., C = 40.5; H = 5.4 per cent.), and by conversion into glutaconic acid by boiling with alkalis.

Δ^2 -cycloPropene-1 : 2-dicarboxylic Acid (IX).

The ethereal washings from the β -hydroxyglutaric acid left on evaporation a cake of crystals consisting chiefly of two acids, Δ^2 -cyclopropene-1 : 2-dicarboxylic acid and glutaconic acid, which were easily separated by crystallising first from ethyl acetate and ultimately from a mixture of acetone and benzene, the cyclopropenedicarboxylic acid being the less soluble. When pure, the cyclopropenedicarboxylic acid separated from ethyl acetate in short needles, m. p. 184° without decomposition (Found: C = 46.8; H = 3.1; M (dihasic) = 128. $C_5H_4O_4$ requires C = 46.9; H = 3.1 per cent.; M = 128).

The acid seemed to possess little tendency to pass into an anhydride on treatment with acetyl chloride; however, it instantly reduced cold alkaline permanganate and on reduction by hydriodic acid and phosphorus yielded *trans*-cyclopropane-1 : 2-dicarboxylic acid (below). On boiling with very concentrated methyl-alcoholic potassium hydroxide, it underwent ring-fission, yielding α -keto-glutaric acid (compare p. 2019).

Glutaconic Acid (V).

The more soluble acid accompanying the cyclopropenedicarboxylic acid proved to be glutaconic acid, which, after purification, had the correct melting point (135 – 136°) and properties.

In addition there was obtained from the ultimate residues a syrup, which showed no tendency to crystallise and was too small in quantity to be subjected to any kind of systematic separation. Qualitative tests, however, indicated that glutaconic acid was one of the principal constituents, and therefore, in order to obtain an estimate of the amount present, the crude syrup was digested with

acetyl chloride containing 4—5 per cent. of phosphorus trichloride. The crude glutaconic anhydride obtained in this manner was purified by dissolution in cold dilute sodium hydroxide, pouring the solution through a wet filter to remove the suspended oil, and regeneration by adding hydrochloric acid, and was finally converted into the anilic acid by treatment with aniline. The same anilic acid was produced when the crystalline glutaconic acid (above) was treated in a similar manner. It melted at 134° and was evidently the *cis*-isomeride (Found: C = 64.4; H = 5.4. Calc., C = 64.4; H = 5.4 per cent.), since on heating it yielded the *trans*-modification (m. p. 167°), which was identified by comparison with an authentic specimen.

trans-cycloPropane-1 : 2-dicarboxylic Acid (XXV).

The aqueous filtrate from the copper salts was worked up for acid products in the usual manner, ether being used as solvent. The excess of acetic acid (derived from the copper acetate) having been removed in a vacuum over solid potassium hydroxide, the syrupy mixture of acids, which had become brown and slightly cloudy owing to partial crystallisation, was esterified with methyl alcohol (3 parts) and sulphuric acid (2 parts), and the esters precipitated by adding water were divided into neutral and acidic fractions by means of ether and sodium carbonate. The acid esters were then re-esterified by the same method and the neutral esters obtained in this way combined with the original neutral product and distilled under reduced pressure. The main portion of the distillate was obtained as a colourless oil, b. p. $125\text{--}140^{\circ}/25\text{ mm.}$, but although it was obviously a mixture, the quantity was insufficient for separation by fractional distillation to be possible. However, from the dark coloured residue in the distilling flask, by treatment with methyl alcohol in the presence of charcoal was obtained a crystalline substance, m. p. 141° , which was identified as methyl pyromellitate by analysis (Found: C = 53.9; H = 4.5. Calc., C = 54.2; H = 4.5 per cent.), and by hydrolysing it to the free acid.

The more volatile esters, b. p. $125\text{--}140^{\circ}/25\text{ mm.}$, were completely hydrolysed by boiling with concentrated (20 per cent.) hydrochloric acid until no more methyl alcohol was liberated. The syrup obtained on evaporation showed little tendency to crystallise, but it gave a red coloration with ferric chloride and on further examination was proved to contain a considerable amount of α -ketoglutaric acid. This was, therefore, removed as completely as possible in the form of its phenylhydrazone and the remaining acids were recovered in

the usual manner and freed from adhering acetic acid by evaporation over potassium hydroxide. In the course of a few weeks the product became largely crystalline and was spread on porous plates to drain off the remaining syrup, the last traces of which, along with a small quantity of a crystalline acid (believed to be glutaric acid) were removed by triturating with warm benzene. The examination of the crystalline material was attended with some difficulty, but it was ultimately shown to consist of a mixture of Δ^2 -cyclopropene-1:2-dicarboxylic acid and *trans*-cyclopropane-1:2-dicarboxylic acid together with at least one other crystalline acid (possibly succinic acid), which could not be definitely identified. All three substances melted in the neighbourhood of 180° and possessed similar solubilities in the usual solvents, and although in preliminary experiments the cyclopropene- and cyclopropane-dicarboxylic acids were obtained in the pure condition by fractionally crystallising the mixture, it was afterwards found to be a more satisfactory method of separation to precipitate the copper salt of the cyclopropanedicarboxylic acid in the presence of 5—10 per cent. of acetone and recover the cyclopropanedicarboxylic acid from the filtrate. After purification by crystallising from water, the acid melted at 175° and was identified by direct comparison with a known specimen as *trans*-cyclopropane-1:2-dicarboxylic acid (Found: C = 46.2; H = 4.8. Calc., C = 46.1; H = 4.6 per cent.).

The yields of the seven acids obtained in this experiment are given in Table I.

(C) *Action of Concentrated Alkalis on $\alpha\beta$ -Dibromoglutaric Acid: Formation of $\alpha\beta$ -Dihydroxyglutaric Acid, Glutaconic Acid, β -Hydroxyglutaric Acid, Glutaric Acid, α -Ketoglutaric Acid, cycloPropenedicarboxylic Acid, cis- and trans-cycloPropane-dicarboxylic Acid, Succinic Acid, and Pyromellitic Acid.*

Fifty grams of $\alpha\beta$ -dibromoglutaric acid (section A) were added as rapidly as possible to 310 c.c. of a boiling 6*N*-methyl-alcoholic solution of potassium hydroxide. When the violence of the reaction had subsided, the product was heated for thirty minutes, evaporated with water, and then rendered acid by means of concentrated hydrochloric acid. The acid products were extracted by ether and acetone as in the preceding experiment, but in this instance almost the whole of the material passed into the ethereal extract, and the acetone solution yielded only a very small amount of $\alpha\beta$ -dihydroxyglutaric acid and some unidentified gummy material.

A considerable quantity of pyromellitic acid crystallised from the ethereal extract on rubbing with a little water, and from the syrupy residue α -ketoglutaric acid, $\alpha\beta$ -dihydroxyglutaric acid, β -hydroxy-

glutaric acid, glutaconic acid, and cyclopropenedicarboxylic acid were separated by a series of processes closely similar to that already described up to the stage at which the unresolved residue was esterified with methyl alcohol. By this means the last trace of pyromellitic acid was removed in the form of its relatively non-volatile methyl ester and the remaining acids were freed from the dark coloured impurities which had been formed in the original reaction and had concentrated in the course of the separation. The colourless syrup obtained on hydrolysing the distilled methyl esters by hydrochloric acid was treated, in the first place, with phenylhydrazine acetate, whereby a certain quantity of α -keto-glutaric acid was precipitated as its phenylhydrazone, and then, after removing the excess of phenylhydrazine, with cupric acetate, the solution being concentrated suitably in order to render the precipitation of the copper salt of cyclopropenedicarboxylic acid as complete as possible. It was found necessary also to boil the suspension in order to lessen the co-precipitation of other substances. Ultimately, the filtrate was worked up for the acids present, which were obtained, finally, in a concentrated solution in acetic acid (derived from the copper and phenylhydrazine acetates). This solution was boiled for two hours with three times its volume of acetyl chloride and the product evaporated in a vacuum over potassium hydroxide. The partly crystalline residue was dissolved in ether and quickly washed with cold dilute sodium hydrogen carbonate solution. The aqueous layer, on acidification, yielded *trans*-cyclopropane-1:2-dicarboxylic acid, but the ethereal solution, on evaporation, left a colourless syrup, which, however, on boiling and finally evaporating with water, gave a wholly crystalline product weighing about 1 gram.

cis-cycloPropane-1:2-dicarboxylic Acid (XXV).

The crystalline mixture of acids had no definite melting point and was therefore fractionally extracted with dry ether until a sparingly soluble residue, m. p. 136—138°, was obtained. This was crystallised for analysis from a mixture of ethyl acetate and benzene and was identified as *cis*-cyclopropane-1:2-dicarboxylic acid (Found: C = 45.9; H = 4.7. Calc., C = 46.1; H = 4.6 per cent.) by comparison with a known specimen of this substance and by conversion into its anhydride (m. p. 59°).

Succinic Acid (XXI).

The acids extracted by boiling ether were recovered by evaporation of the solvent and extracted by means of hot benzene. The insoluble

portion melted indefinitely between 165° and 180°, but after one crystallisation from water it melted quite sharply at 184° and was identified as succinic acid by comparison with a genuine specimen (Found: C = 40.3; H = 5.1. Calc., C = 40.7; H = 5.1 per cent.).

Glutaric Acid (XXVI).

The material extracted by boiling benzene consisted essentially of glutaric acid. In the crude condition, it melted at 88–93°, but after it had been crystallised several times from benzene the melting point rose to 94–95°. Identity was established by a mixed-melting-point determination with a genuine specimen of glutaric acid, and by analysis (Found: C = 45.1; H = 6.4. Calc., C = 45.45; H = 6.1 per cent.).

The yields are indicated in Table I.

(D) Action of Dilute Alkalis on Ethyl α -Bromoglutaconate: Formation of α -Ketoglutaric Acid, cycloPropenedicarboxylic Acid, trans-cycloPropenedicarboxylic Acid, and Pyromellitic Acid.

Twenty-five grams of ethyl α -bromoglutaconate (section A) were boiled for twenty hours with 4.5 equivalents of 2*N*-aqueous sodium carbonate. The homogeneous solution was then acidified, saturated with ammonium sulphate, and extracted repeatedly with ether. The syrupy product deposited only a small amount of crystalline material and was therefore esterified with methyl alcohol as described on p. 2016. The major portion of the methyl esters having been distilled at 120–140°/21 mm., there remained a crystalline residue which was easily purified and identified as methyl pyromellitate. The distillate, on hydrolysis by means of hydrochloric acid, yielded a clear, pale yellow syrup, the principal constituent of which was found to be α -ketoglutaric acid, which was isolated as usual as its phenylhydrazone. The remaining acids were then treated with copper acetate in concentrated aqueous solution in order to precipitate the copper salt of cyclopropenedicarboxylic acid and then extracted from the filtrate and treated with acetyl chloride as described on p. 2018, the unchanged acids being separated from the anhydrides by shaking for a few moments with ice-cold dilute sodium hydrogen carbonate. No pure substance was isolated from the anhydrides, but the principal constituent of the unchanged acids proved to be trans-cyclopropane-1:2-dicarboxylic acid, which was readily obtained in the crystalline condition by saturating a concentrated aqueous solution with gaseous hydrogen chloride.

The yields were as stated in Table I.

(E) *Action of Concentrated Alkalis on Ethyl α -Bromoglutaconate: Formation of α -Ketoglutaric Acid, cycloPropenedicarboxylic Acid, cis- and trans-cycloPropanedicarboxylic Acid, Succinic Acid, and Pyromellitic Acid.*

Thirty grams of ethyl α -bromoglutaconate (section A) were heated to 100°, and run in a thin stream into 150 c.c. of a boiling 6N-methyl-alcoholic solution of potassium hydroxide. The mixture was boiled for thirty minutes and then evaporated several times with water. The residue was acidified with concentrated hydrochloric acid and the organic acids were extracted with pure ether.

The product, after keeping for a few days, deposited a considerable quantity of pyromellitic acid, and on adding a small amount of water a further quantity separated. This was collected and the residual brown syrup esterified with methyl alcohol, and the esters distilled and then rehydrolysed as in the preceding experiments. α -Ketoglutaric acid, cyclopropenedicarboxylic acid, and *trans*-cyclopropanedicarboxylic acid were then isolated and obtained in the pure condition exactly as described in the last experiment (section D). The anhydrides corresponding with those which in that instance yielded no recognisable product, in this case gave on rehydration a syrupy mixture of acids, which, in the course of a few months, deposited a relatively considerable quantity of crystals. These were found to consist of approximately equal quantities of *cis*-cyclopropane-1:2-dicarboxylic acid and succinic acid, which, after the syrup had been removed by draining on porous porcelain and washing with hot benzene, were easily separated by means of dry ether as described on p. 2018.

The yields of the various acids isolated are given in Table I, column 4.

(F) *Action of Concentrated Alkalis on Δ^3 -cycloPropene-1:2-dicarboxylic Acid*: Formation of α -Ketoglutaric Acid.*

The cyclopropenedicarboxylic acid was boiled with 6N-methyl-alcoholic potassium hydroxide under conditions closely resembling those employed in the experiments already described (sections D and E). The product was worked up for acids in the usual manner

* This experiment might be regarded as evidence against the constitution proposed for this acid, and it must be confessed that the position of the double bond has not yet been satisfactorily established. From the point of view of the present investigation, however, it matters nothing whether the double bond has or has not passed to the Δ^1 -position, and the question has therefore been left over for future examination.

and the α -ketoglutaric acid separated in the form of its phenylhydrazone.

We are much indebted to Prof. J. F. Thorpe for his interest in this investigation and to the Chemical Society for a grant which has greatly facilitated it.

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CCXXXII.—*Studies in the Dihydronaphthalene Series.*
Part II. The ar-Dihydro- α -naphthols and their Derivatives.

By FREDERICK MAURICE ROWE and ESTHER LEVIN.

OUR investigations of the hydrogenation of α -naphthylamine (T., 1918, 113, 955; *J. Soc. Dyers and Col.*, 1919, 35, 128; *J. Soc. Chem. Ind.*, 1920, 39, 241T; T., 1920, 117, 1574) have shown that the base is converted into *ar*-tetrahydro- α -naphthylamine by the action of sodium and amyl alcohol, but that when the reduction is effected under suitable conditions with sodium and ethyl alcohol in the presence of an inert solvent of high boiling point, such as solvent naphtha or toluene, the intermediate 5:8-dihydro- α -naphthylamine only is obtained. The latter is isomerised by the action of sodium ethoxide at a suitable temperature and concentration to 5:6(or 7:8)-dihydro- α -naphthylamine, a compound which differs from its isomeride in that it may be converted into the tetrahydro-derivative by the action of sodium and ethyl alcohol.

In the case of α -naphthol also the action of sodium and amyl alcohol leads to the formation of the *ar*-tetrahydro-derivative (Bamberger and Bordt, *Ber.*, 1890, 23, 215; Jacobson and Turnhull, *ibid.*, 1898, 31, 897). The *ar*-dihydro- α -naphthols corresponding with the two *ar*-dihydro- α -naphthylamines have not been described hitherto, and it appeared of interest, therefore, to prepare and examine these compounds.

In the first place, attempts were made to prepare these compounds by the direct hydrogenation of α -naphthol in a similar manner to that used for the preparation of the dihydro- α -naphthylamines (*loc. cit.*), with the exception that an increased quantity of sodium

was employed on account of the acidic nature of the product. The reduction mixture was diluted and distilled in a current of steam to remove the volatile solvent. The residue was then acidified, distilled in a current of steam, and the distillate examined.

(a) When α -naphthol, ethyl alcohol, toluene or solvent naphtha, and sodium were employed, the distillate contained a product, melting at 56° , which proved to be a mixture of 5:8-dihydro- α -naphthol and 5:6(or 7:8)-dihydro- α -naphthol, together with a small quantity of unreduced α -naphthol.

(b) When α -naphthol, ethyl alcohol, solvent naphtha or toluene, and sodium were employed, and the mixture, after all the sodium had disappeared, was distilled slowly to remove the volatile solvent, and then heated for one hour at 125° , the product proved to be a mixture of 5:6(or 7:8)-dihydro- α -naphthol with some unreduced α -naphthol. Separation of this mixture was at first effected by means of fractional distillation in a current of steam, as the hydrogenated naphthol is more volatile than α -naphthol, but later, when it was found that the hydrogenated naphthol did not form a picrate, it proved more satisfactory to remove the α -naphthol from the mixture by conversion into the picrate. 5:6(or 7:8)-Dihydro- α -naphthol forms colourless plates or needles, melting at 71° .

As a result of these experiments it appears that, in the case of α -naphthol, it is more difficult to determine conditions suitable for the preparation of the 5:8-dihydro-derivative than is the case with α -naphthylamine, for, although the conditions were varied, in all cases where hydrogenation occurred, the product was a mixture of the two dihydro- α -naphthols, owing to the fact that some of the 5:8-dihydro-derivative was isomerised during the reaction. This is, however, not surprising, for in view of the increased concentration of alkali used in these experiments, it is probable that conditions which are favourable for the hydrogenation of α -naphthol to its 5:8-dihydro-derivative are equally favourable for the isomerisation of this compound to the 5:6(or 7:8)-dihydro- α -naphthol.

Therefore, whilst the method (b) outlined above was suitable for the preparation of 5:6(or 7:8)-dihydro- α -naphthol, the method (a) was unsuitable for the preparation of the 5:8-derivative, as we were unable to separate the mixture of the two dihydro-compounds formed.

Attention was next directed to the preparation of the dihydro- α -naphthols from the corresponding amines by diazotisation and boiling the diazonium compound.

It is noteworthy that whilst this method gives good results in the case of the preparation of *ar*-tetrahydro- α -naphthol from *ar*-tetrahydro- α -naphthylamine (Bamberger and Althausse, *Ber.*, 1888,

21, 1892), the yields of the dihydro- α -naphthols from the corresponding dihydro-amines are low, and these compounds are always formed together with a considerable proportion of naphthalene.

5:8-Dihydro- α -naphthol forms colourless plates or needles, melting at 75°, with a pronounced phenolic odour, whilst 5:6- or 7:8-dihydro- α -naphthol also forms colourless plates or needles, melting at 71°, identical with the product previously described and obtained by the direct hydrogenation of α -naphthol and isomerisation of the intermediate 5:8-dihydro- α -naphthol.

The following table indicates the behaviour of aqueous solutions of α -naphthol, 5:8-dihydro- α -naphthol, 5:6(or 7:8)-dihydro- α -naphthol, and *ar*-tetrahydro- α -naphthol on the addition of ferric chloride and calcium hypochlorite respectively:

	α -Naphthol.	5:8-Dihydro- α -naphthol.	5:6(or 7:8)- Dihydro- α -naphthol.	<i>ar</i> -Tetrahydro- α -naphthol.
Ferric chloride.	Violet colour and precipitate.	A more reddish-violet colour and precipitate which develops more slowly than is the case with α -naphthol.	Brown colour and precipitate.	Yellow colour and precipitate.
Calcium hypochlorite.	" "	A much redder colour and precipitate than with α -naphthol.	" "	Faint white precipitate.

An important difference in the properties of 5:8-dihydro- α -naphthol and 5:6(or 7:8)-dihydro- α -naphthol is shown by their behaviour on treatment with sodium and ethyl alcohol, for the 5:8-isomeride remains unchanged, whilst the 5:6(or 7:8)-isomeride is converted into *ar*-tetrahydro- α -naphthol.

It is clear, therefore, that the course of the reaction in the conversion of α -naphthol into *ar*-tetrahydro- α -naphthol by means of sodium and an alcohol is completely analogous to the course of the reactions in the hydrogenation of naphthalene and α -naphthylamine under similar conditions, and the intermediate dihydro-derivatives in each case exhibit a similar behaviour when treated with sodium and ethyl alcohol.

The behaviour of the two dihydro- α -naphthols when sulphonated and nitrated under conditions similar to those employed for *ar*-tetrahydro- α -naphthol (*loc. cit.*) was next examined. When the dihydro- α -naphthols are treated with twice their weight of concentrated sulphuric acid for two days at the ordinary temperature,

they are converted, for the greater part, into water-soluble products, although sulphonation is accompanied to a certain extent by resinification. The crude sodium salts of the sulphonic acids could be isolated from the sulphonation mixtures in the usual manner. The sulphonic acids are readily hydrolysed by dilute acids with regeneration of the dihydro- α -naphthols. From analogy to the monosulphonic acid of *ar*-tetrahydro- α -naphthol it was to be expected that the sulphonic group would enter the *para*-position with respect to the hydroxyl group in the dihydro- α -naphthols, and that this was the case is obvious from the behaviour of the sulphonic acids on nitration.

5 : 8-Dihydro- α -naphthol-4-sulphonic acid and 5 : 6(or 7 : 8)-dihydro- α -naphthol-4-sulphonic acid possess similar properties to *ar*-tetrahydro- α -naphthol-4-sulphonic acid, and, for example, in alkaline solution do not combine with diazonium compounds to form azo-dyes.

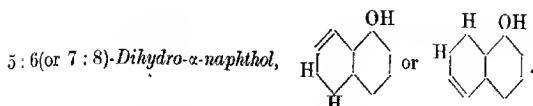
For the nitration experiments it is unnecessary to isolate the sulphonic acids, but the diluted sulphonation mixtures were nitrated directly, and 2-nitro-5 : 8-dihydro- α -naphthol, yellow needles, melting at 98°, volatile with steam, 2-nitro-5 : 6(or 7 : 8)-dihydro- α -naphthol, yellow needles, melting at 55°, volatile with steam, and 2 : 4-dinitro-5 : 8-dihydro- α -naphthol, yellow, prismatic needles, melting at 127°, were obtained.

Both dihydro- α -naphthols exhibited behaviour similar to that of *ar*-tetrahydro- α -naphthol when treated with nitrous acid, and yielded 4-nitro-5 : 8-dihydro- α -naphthol, brown needles, melting at 161°, and 4-nitro-5 : 6(or 7 : 8)-dihydro- α -naphthol, yellow needles, melting at 162°, respectively.

All attempts to obtain 2 : 4-dinitro-5 : 6(or 7 : 8)-dihydro- α -naphthol either by nitration of the dihydronaphtholsulphonic acid with two molecules of nitric acid or by the further nitration of 4-nitro-5 : 6(or 7 : 8)-dihydro- α -naphthol with nitric acid resulted in complete resinification of the compound.

It should be noted that whereas the nitration of *ar*-tetrahydro- α -naphthol under the conditions described results in almost theoretical yields of the nitro-derivatives in all cases, the dihydro- α -naphthols are, on nitration, more readily oxidised under the existing conditions, and give extremely low yields of the nitro-derivatives. This behaviour is not surprising, however, in view of the unsaturated character of the hydrogenated ring in the dihydro- α -naphthols.

EXPERIMENTAL.

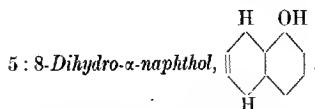


(1) A mixture of 400 c.c. of dry toluene or solvent naphtha (b. p. 139°) and 70 grams of sodium was boiled in a flask fitted with a reflux condenser, and a solution of 30 grams of α -naphthol in rather more ethyl alcohol than is necessary to dissolve the sodium was added drop by drop through the condenser. Boiling was continued until all the sodium had disappeared, and the mixture was then distilled until the internal temperature rose to 125°, at which temperature heating was continued for one hour. The mixture was poured into water and distilled in a current of steam to remove the remainder of the toluene. The residue was acidified with hydrochloric acid and distilled in a current of steam. The distillate was saturated with sodium chloride, as the dihydronaphthol is appreciably soluble in water, and the crystalline product separated. Any unaltered α -naphthol was removed by conversion into its picrate.

5:6(or 7:8)-*Dihydro- α -naphthol* forms colourless, silky needles or plates, melting at 71° (corr.) (Found: C = 82.19; H = 6.79. $C_{10}H_{10}O$ requires C = 82.19; H = 6.85 per cent.).

(2) Fifteen grams of 5:6(or 7:8)-dihydro- α -naphthylamine were stirred into 25 grams of sulphuric acid diluted with 100 c.c. of water, and the crystalline paste, cooled to 2°, was diazotised with a solution of 7.2 grams of sodium nitrite in 100 c.c. of water. The yellowish-red solution was kept for half an hour, warmed gently until the evolution of nitrogen ceased, distilled in a current of steam, and the distillate saturated with sodium chloride. The product, a mixture of 5:6(or 7:8)-dihydro- α -naphthol and naphthalene, was extracted with sodium hydroxide, the extract was acidified, and the regenerated dihydronaphthol purified by distillation in a current of steam. The product was identical with that obtained by the direct hydrogenation of α -naphthol (Found: C = 81.99; H = 6.66 per cent.).

ar-Tetrahydro- α -naphthol is readily obtained from 5:6 (or 7:8)-dihydro- α -naphthol by the gradual addition of 30 grams of sodium to a boiling solution of 10 grams of this dihydro- α -naphthol in 400 c.c. of dry ethyl alcohol. The *ar*-tetrahydro- α -naphthol was isolated in the usual manner.



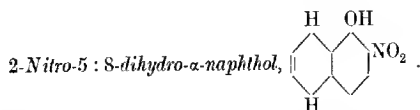
This compound was prepared from 5 : 8-dihydro- α -naphthylamine in a similar manner to that described for the preceding compound. 5 : 8-Dihydro- α -naphthol forms colourless plates or needles, melting at 75° (Found: C = 81.99; H = 6.92. $\text{C}_{10}\text{H}_{10}\text{O}$ requires C = 82.19; H = 6.85 per cent.). When heated with a solution of sodium ethoxide, it is converted into 5 : 6 (or 7 : 8)-dihydro- α -naphthol.

Sulphonation of 5 : 8-Dihydro- α -naphthol.

Ten grams of finely powdered 5 : 8-dihydro- α -naphthol having been completely dissolved in 20 grams of cold concentrated sulphuric acid, the solution was kept for two days at the ordinary temperature, and the mixture was then diluted with water and filtered from a trace of unsulphonated 5 : 8-dihydro- α -naphthol. The filtrate was neutralised with milk of lime, and the calcium salt, after removal of calcium sulphate, was converted into the sodium salt and evaporated to dryness. The sodium salt could not be obtained in a pure condition for analysis owing to the presence of resinous matter. It is very readily soluble in water, and the sulphonic group is readily hydrolysed by boiling with dilute acids, 5 : 8-dihydro- α -naphthol being regenerated. 5 : 8-Dihydro- α -naphthol-4-sulphonic acid, in neutral or alkaline solution, does not couple with diazonium salts to form azo-compounds.

Sulphonation of 5 : 6(or 7 : 8)-Dihydro- α -naphthol.

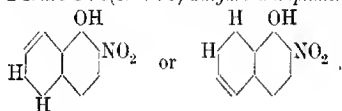
This sulphonation was effected in a similar manner to that described for the preceding compound. The product, which could not be obtained in a sufficiently pure condition for analysis, possesses similar properties to those of its isomeric.



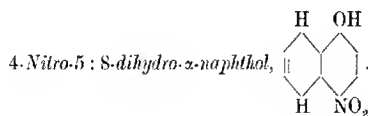
Two grams of 5 : 8-dihydro- α -naphthol were dissolved in 4 grams of cold concentrated sulphuric acid. The solution was allowed to

remain for two days, diluted with 6.5 c.c. of water, cooled in ice and nitrated with 0.9 c.c. of nitric acid (*d* 1.4; 1 mol.) diluted with 2 c.c. of water. The nitrosulphonic acid did not separate from the mixture as did the corresponding compound during the nitration of *ar*-tetrahydro- α -naphthol-4-sulphonic acid under the same conditions. The nitrosulphonic acid, therefore, was not isolated in this case, but the nitration mixture was boiled with dilute sulphuric acid (1 : 1) in order to hydrolyse the sulphonic group, and then distilled in a current of steam. 2-Nitro-5 : 8-dihydro- α -naphthol forms yellow needles, melting at 98°. It is readily volatile with steam and possesses a sweet, pleasant odour. It dissolves in sodium hydroxide solution with an orange coloration, forms an orange-red sodium salt, and couples with diazonium compounds forming azo-dyes (Found: C = 62.71; H = 4.80; N = 7.13. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).

2-Nitro-5 : 6(or 7 : 8)-dihydro- α -naphthol,



This compound was prepared in the same manner as that described for the preceding compound. It forms yellow needles, melting at 55°, and possesses similar properties to those of 2-nitro-5 : 8-dihydro- α -naphthol (Found: C = 62.71; H = 4.84; N = 7.50. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).

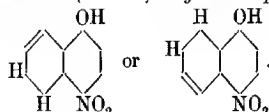


Five grams of 5 : 8-dihydro- α -naphthol were dissolved in sodium hydroxide, the solution being diluted with water to 150 c.c. To this, an aqueous solution of 3.6 grams of sodium nitrite (2 mols.) was added together with 100 grams of ice. Fifty c.c. of 10 per cent. sulphuric acid contained in a dropping funnel, the end of which dipped below the surface of the liquid, were then slowly run into the mixture with constant agitation. The sticky, yellowish-white precipitate was collected and washed with cold water. The major portion dissolved in sodium carbonate solution, and was filtered from a quantity of a tarry residue. From the filtrate, the

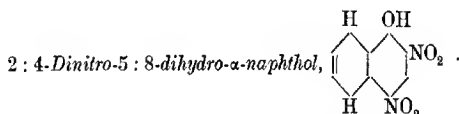
3 z*

product was precipitated by dilute acetic acid. 4-Nitro-5:8-dihydro- α -naphthol crystallises from dilute alcohol in brown needles, melting at 161° (with decomp.). It is not volatile with steam. It dissolves in sodium hydroxide solution with a yellowish-brown coloration, and on addition of excess of alkali, the sodium salt crystallises in brown needles. 4-Nitro-5:8-dihydro- α -naphthol does not couple with diazonium compounds (Found: C = 62.79; H = 4.78; N = 7.15. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).

4-Nitro-5:6(or 7:8)-dihydro- α -naphthol,



This compound was prepared in the same manner as that described for the preceding compound. It crystallises from dilute alcohol in yellow needles, melting at 162° (with decomp.). Its properties are similar to those of 4-nitro-5:8-dihydro- α -naphthol (Found: C = 62.99; H = 4.75; N = 7.15. $C_{10}H_9O_3N$ requires C = 62.82; H = 4.71; N = 7.33 per cent.).



Four grams of 5:8-dihydro- α -naphthol were dissolved in 8 grams of cold concentrated sulphuric acid, the solution was allowed to remain for two days, and diluted with 10 c.c. of water. The clear liquid was cooled in ice, and nitrated with 4.7 c.c. of nitric acid (*d* 1.4; 2.5 mols.) diluted with 5.5 c.c. of water. After all the nitric acid had been added, the mixture was allowed to remain at the ordinary temperature for some time. It was then warmed on the water-bath at 50° until a semi-crystalline product, insoluble in water, had separated. A quantity of resinous impurity was removed from the product by careful washing with cold toluene.

2:4-Dinitro-5:8-dihydro- α -naphthol crystallises from ether in long, yellow, prismatic needles, melting at 127°. It dissolves in sodium hydroxide solution with an orange-brown coloration, and the sodium salt crystallises from the solution in orange needles

(Found : C = 50.75; H = 3.36; N = 11.99. $C_{10}H_8O_5N_2$ requires C = 50.85; H = 3.39; N = 11.87 per cent.).


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CCXXXIII.—*Researches on Sulphuryl Chloride. Part I.* *Influence of Catalysts : a Convenient Method of* *Chlorinating Benzene.*

By OSWALD SILBERRAD.

THE present investigation was instituted with the two-fold object of devising a convenient method of chlorinating the less reactive benzenoid hydrocarbons with sulphuryl chloride and also of throwing additional light on chlorination generally. Heretofore sulphuryl chloride has been little used for the chlorination of such compounds owing to the difficulty with which it reacts; thus Dubois (*Zeitsch. Chem. von Beilstein u. Fritz Hubner*, 1866, **2**, 705) found it necessary to heat it at 150° in sealed tubes with benzene in order to effect chlorination, whilst Töhl and Eberhard (*Ber.*, 1893, **26**, 2941) found 160 — 170° necessary. The present investigation has, however, shown that in the presence of suitable catalysts this hydrocarbon may be chlorinated in a few minutes at the ordinary temperature (for details see below, experiments Nos. 6, 7, 8, and 9), and, further, that in all cases where rapid chlorination is induced the reaction is accompanied by the formation of intensely coloured intermediate

compounds probably of the type , thus giving inter-

esting evidence respecting the additive theory of chlorination (compare Kekulé, *Annalen*, 1858, **106**, 129; Michael, *J. pr. Chem.*, 1883, [ii], **37**, 486; van't Hoff, "Ansichten über Organische Chemie," I, 223, 244; Schmidlin and Lange, *Ber.*, 1910, **43**, 2806; 1912, **45**, 1899).

Broadly speaking, the catalysts investigated divide themselves into two groups, namely, those dependent on the liberation of free chlorine due to the dissociation of the sulphuryl chloride, and those the action of which involves the formation of some intensely coloured intermediate compound, to which there is every reason to assign a structure of the type indicated above (compare H. E. Armstrong, *P.*, 1888, **4**, 27).

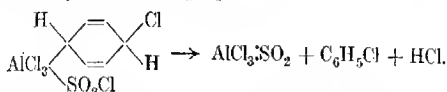
Of the first group of catalysts investigated, iodine induces chlorination to the extent of 17 per cent. on boiling for eight hours;* thionyl chloride 24 per cent. in the same time; sulphur or sulphur chloride 37 per cent., and ferric chloride 53 per cent.† The reason for this wide difference in velocity becomes evident on considering the properties of an admixture of the reacting substances with sulphuryl chloride. Iodine acts as a simple carrier dependent on the dissociation of sulphuryl chloride for the formation of iodine trichloride (compare Ruff, *Ber.*, 1901, **34**, 1749). Thionyl chloride has been shown to behave as a mixture of sulphur dioxide and sulphur tetrachloride under certain conditions (Prinz, *Annalen*, 1884, **223**, 355); it therefore appears probable that the latter compound is the active chlorinating agent in this case and also when sulphur or sulphur chloride is present, both of which are converted into higher chlorides by excess of sulphuryl chloride (Ruff, *loc. cit.*, p. 1750). Ferric chloride acts, not only as a carrier, but also, as is often the case with this reagent, in a manner similar to aluminium chloride by inducing dissociation of the sulphuryl chloride (compare Ruff, *Ber.*, 1902, **35**, 4453; *Chem. Zeit.*, 1906, **30**, 1225; Roland, *Chem. Zeit.*, 1906, **30**, 1173).

The second series of catalysts differs materially from those considered above in that their action is accompanied by the production of much more intensely coloured substances, and also in that they induce incomparably more vigorous chlorination. They consist of aluminium chloride together with some sulphur compound, the simplest case being when sulphuryl chloride itself acts in this capacity also. In this connexion it should be observed that the action of aluminium chloride on a mixture of sulphuryl chloride and benzene under conditions conducive to the Friedel and Crafts reaction has already been investigated by Töhl and Eberhard (*loc. cit.*), who, working under these conditions, obtained chiefly benzenesulphonyl chloride together with a smaller quantity of diphenylsulphone and about $4\frac{1}{2}$ per cent. of chlorobenzene; this work was subsequently confirmed and elaborated by Böcsken (Rec. trav. chim., 1911, **30**, 381), who, working under conditions even more suited to the Friedel and Crafts reaction, succeeded in isolating benzenesulphinic acid as well as the above compounds.

* Töhl and Eberhard (*Ber.*, 1893, **26**, 2941) obtained chlorobenzene by heating a mixture of benzene with sulphuryl chloride and iodine at 150° in sealed tubes. D.R.-P. 269249, which relates to the chlorination of 3-methyl-anthraquinone by means of sulphuryl chloride in the presence of nitrobenzene, also claims the use of iodine as a catalyst.

† Quite recently Durrans made use of ferric chloride in effecting the chlorination of triphenyl phosphate, which is not attacked by sulphuryl chloride alone (private communication).

When, however, sulphuryl chloride is rapidly run into a boiling mixture of benzene and aluminium chloride, chlorination occurs almost to the exclusion of all other reactions, the yield being about 90 per cent. of the theoretical, whilst the reacting mass, which at first assumes a vandyke-brown hue, subsequently turns to an intense violet-brown. This remarkable reaction appears to be traceable to the tendency of aluminium chloride to form a double compound both with the hydrocarbon and also with the sulphuryl chloride, the probable constitution and decomposition of which may well be indicated by the following equation:



Additional probability is lent to this suggestion by the fact that the reaction becomes vigorous at the same temperature at which Ruff observed the compound $\text{AlCl}_3 \cdot \text{SO}_2$ to break up with regeneration of the aluminium chloride (*Ber.*, 1902, **35**, 4453). The addition of thionyl chloride to the above mixture materially reduces the temperature at which the action takes place, whilst the presence of sulphur or sulphur chloride brings about vigorous chlorination in the cold, the end product being in this case intensely indigo-blue. The constitution of this coloured compound is probably similar to that suggested above; the precise nature is, however, still under investigation.

EXPERIMENTAL.

In order to avoid repetition, the method adopted in investigating the influence of the various catalysts examined on the chlorination of benzene with sulphuryl chloride is here briefly set forth in general terms: The required hydrocarbon (156 grams of benzene; 2 mols.), together with the catalyst in question, was placed in a flask submerged in a water-bath and provided with an efficient reflux condenser, the upper portion of which was loosely packed with asbestos and connected through a trap with a flask containing 10 litres of water in order to absorb the sulphur dioxide and hydrochloric acid gas which are copiously evolved during the reaction. A 5 per cent. excess of sulphuryl chloride (284 grams) was then run in, the water-bath being maintained at such a temperature that a vigorous reaction occurred, or, in the event of no vigorous action taking place, at the boiling point of the mixture. The reaction was allowed to proceed for eight hours, except in such cases as it was complete in a shorter time. The product was then freed from any remaining sulphuryl chloride by agitation with

water, steam-distilled, and the relative degree of chlorination ascertained by determining the density of the distillate; from the figure thus obtained the composition was calculated on the assumption that the product consisted of a mixture of chlorobenzene together with unaltered benzene, or dichlorobenzene, as the case might be: the exact nature of the constituents was subsequently established by submitting the steam-distillate to systematic fractionation and identifying the products isolated in the usual manner. Operating in this way, the influence of the following catalysts was examined with the following results:

Experiment No. 1. Catalyst Iodine.

Reaction.—On mixing the ingredients (benzene, 156 grams; sulphuryl chloride, 284 grams; iodine, 5 grams), no reaction occurs; on boiling, the red coloration due to iodine slowly disappears as the iodine is converted into the trichloride, and the liquid assumes a ruddy brown colour. During the whole experiment a slow, steady stream of sulphur dioxide and hydrochloric acid gas is evolved: the reaction is evidently not completed by boiling for the duration of the experiment, namely, eight hours.

Yield.—On steam distillation an oil (148 grams) having d_{20}^{25} 0.927 was obtained; this corresponds with a yield of 38 grams of chlorobenzene, from which it would appear that iodine induces the chlorination of 16.8 per cent. of the benzene in eight hours under the above conditions.

Identification.—10.5 Grams of pure chlorobenzene were isolated by fractionation (Found: Cl = 31.22. Calc., Cl = 31.50 per cent.).

Experiment No. 2. Catalyst Thionyl Chloride.

Reaction.—On mixing the ingredients (benzene, 156 grams; thionyl chloride, 5 grams; sulphuryl chloride, 284 grams), no reaction occurs; on heating, the liquid, which at first is colourless, rapidly assumes a pink shade, and a slow stream of sulphur dioxide and hydrochloric acid gas is evolved; eight hours' boiling fails to complete the reaction.

Yield.—On steam distillation, an oil (163 grams) having d_{20}^{25} 0.945 was obtained; this corresponds with a yield of 54.5 grams of chlorobenzene, hence thionyl chloride induces chlorination to the extent of 24 per cent. of the benzene in eight hours under the above conditions.

Identification.—Thirty-six grams of pure chlorobenzene were isolated on fractionation (Found: Cl = 31.11 per cent.).

Experiment No. 3. Catalyst Sulphur.

Reaction.—On dissolving the sulphur (5 grams) in the benzene (156 grams) and adding the sulphuryl chloride (284 grams), no action occurred in the cold; on boiling, a slow stream of sulphur dioxide and hydrochloric acid gas was evolved and the liquid, which in the first instance possessed a pale lemon tint, gradually assumed a decided amber yellow. The reaction was not complete at the expiration of eight hours' boiling.

Yield.—On steam distillation, an oil (166 grams) having d_{21}^{20} 0.978 was obtained. This corresponds with a yield of 83 grams of chlorobenzene, hence sulphur under the above conditions induces chlorination to the extent of 37 per cent. of the benzene used in eight hours.

Identification.—Fifty-one grams of pure chlorobenzene were isolated by fractionation (Found: Cl = 31.13 per cent.).

Experiment No. 4. Catalyst Sulphur Chloride.

Reaction.—On mixing the ingredients together (benzene, 156 grams; sulphuryl chloride, 284 grams; sulphur chloride, 5 grams), there was no action in the cold; on boiling, a slow, steady evolution of sulphur dioxide and hydrochloric acid gas occurred, and the liquid, which at first was pale lemon-yellow, developed a clear amber colour. The reaction was not complete after eight hours boiling.

Yield.—On steam distillation, an oil (160 grams) having d_{21}^{20} 0.985 was obtained. This corresponds with a yield of 84 grams of chlorobenzene, hence sulphur chloride under the above conditions induces chlorination to the extent of 37 per cent. of the benzene used in eight hours.

Identification.—Fifty-four grams of pure chlorobenzene were isolated by fractionation (Found: Cl = 31.28 per cent.).

Experiment No. 5. Catalyst Ferric Chloride.

Reaction.—On mixing the ingredients (benzene, 156 grams; sulphuryl chloride, 284 grams; anhydrous ferric chloride, 5 grams), no reaction occurred in the cold; on boiling, a stream of sulphur dioxide and hydrochloric acid gas was evolved; the reaction was evidently not completed at the expiration of eight hours at the boiling point of the mixture. During the operation the product turned through amber yellow to a ruddy brown.

Yield.—On steam distillation, an oil (174 grams) having d_{21}^{20}

1.024 was obtained; this corresponds with a yield of 119 grams of chlorobenzene, from which it would appear that ferric chloride induces chlorination to the extent of 53 per cent. of the benzene in eight hours under the above conditions.

Identification.—Ninety grams of pure chlorobenzene were isolated on fractionation (Found : Cl = 31.36 per cent.), also 2 grams of *p*-dichlorobenzene, m. p. 53°.

Experiment No. 6. Catalyst Aluminium Chloride (Anhydrous).

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; anhydrous aluminium chloride, 5 grams.

Reaction.—The benzene and aluminium chloride were mixed, a few c.c. of sulphuryl chloride added, and the temperature of the bath raised until the slight reaction which started in the cold became vigorous—this occurred at 60–70°, at which temperature the remainder of the sulphuryl chloride was rapidly added. During the operation, which occupied forty-five minutes and was accompanied by the copious evolution of sulphur dioxide and hydrochloric acid gas, the mixture, which on the first addition of sulphuryl chloride assumed a deep vandyke-brown colour, passed through black to intense violet-brown, the precise shade of which varied considerably when benzene containing thiophen or traces of toluene was used.

Yield.—On steam distillation, an oil (200 grams) having d_{44}^{20} 1.105 was obtained; this corresponds with 199 grams of chlorobenzene, or a yield amounting to 89 per cent. of the theoretical.

Identification.—One hundred and eighty-one grams of pure chlorobenzene were isolated on fractionation (Found : Cl = 31.48 per cent.).

Experiment No. 7. Catalyst Aluminium Chloride and Thionyl Chloride.

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; aluminium chloride, 5 grams; thionyl chloride, 1 gram.

Reaction.—On adding the thionyl chloride to the benzene and aluminium chloride, which had been previously mixed, the liquid turned dark brown and, on adding the sulphuryl chloride to this mixture, a fairly vigorous reaction set in at the ordinary temperature; the operation was completed by warming at 80° and occupied in all forty-five minutes, the final product being intensely violet-brown. The reaction was considerably more vigorous than when aluminium chloride alone formed the catalyst (No. 6).

Yield.—On steam distillation, an oil (200 grams) having d_{44}^{20}

1.121 was obtained: this corresponds with 186 grams of chlorobenzene and 14 grams of dichlorobenzene, from which it would appear that 83 per cent. of the available chlorine had passed into the hydrocarbon.

Identification.—One hundred and fifty-two grams of pure chlorobenzene were isolated on fractionation (Found: Cl = 31.62 per cent.), also 5 grams of *p*-dichlorobenzene, m. p. 53°.

Experiment No. 8. Catalyst Aluminium Chloride and Sulphur.

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; aluminium chloride, 5 grams; sulphur, 1 gram.

Reaction.—The sulphur was dissolved in the benzene, the aluminium chloride added, and a few c.c. of sulphuryl chloride run in; the temperature of the bath was then raised until the slight reaction which started in the cold became vigorous, which occurred at about 49°, at which temperature the remainder of the sulphuryl chloride was added. The whole operation occupied fifty-five minutes, during which time the liquid assumed first a vandyke-brown colour, then black, and finally pure indigo-blue. In carrying out this operation, it is important that the sulphur be completely in solution before starting, as otherwise the reaction may be delayed in starting and subsequently become uncontrollable.

Yield.—On steam distillation, an oil (187 grams) having d_{20}^{20} 1.156 was obtained; this corresponds with 143 grams of chlorobenzene and 44 grams of dichlorobenzene, from which it would appear that 89 per cent. of the available chlorine has passed into the hydrocarbon.

Identification.—One hundred and twenty grams of pure chlorobenzene were obtained by fractionation (Found: Cl = 31.55 per cent.), also 15 grams of *p*-dichlorobenzene, m. p. 53°.

Experiment No. 9. Catalyst Aluminium Chloride and Sulphur Chloride.

Ingredients.—Benzene, 156 grams; sulphuryl chloride, 284 grams; aluminium chloride, 5 grams; sulphur chloride, 1 gram.

Reaction.—On adding the sulphur chloride to the mixture of benzene and aluminium chloride, the liquid turned deep green, which changed to bluish-black as soon as the sulphuryl chloride was added, and so vigorous a reaction set in that the temperature of the surrounding bath, which at the beginning of the experiment stood at 20°, rose 10° during the addition of this compound. The reaction was complete in thirty minutes, the product being intensely blue.

Yield.—On steam distillation, an oil (183 grams) having d_{4}^{20} 1.137 was obtained; this corresponds with a yield of 156 grams of chlorobenzene and 27 grams of dichlorobenzene, from which it would appear that 87 per cent. of the available chlorine has passed into the hydrocarbon.

Identification.—One hundred and thirty grams of pure chlorobenzene were isolated by fractionation (Found: Cl = 31.82 per cent.), also 7 grams of *p*-dichlorobenzene, m. p. 53°.

The author's thanks are due to Messrs. A. Boake, Roberts and Co., Ltd., for supplying the sulphuryl chloride required for this investigation.

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CCXXXIV.—*The Adsorption of Thorium-B and Thorium-C by Ferric Hydroxide.*

By JOHN ARNOLD CRANSTON and ROBERT ALEXANDER BURNETT.

It has been found by McCoy and Viol (*Phil. Mag.*, 1913, [vi], 25, 340) that "ferric iron precipitated by fumaric acid from a boiling, nearly neutral solution of thorium-*B* and thorium-*C* carries down all the -*C* and only a small part of the -*B*." By redissolving the precipitated iron with the radioactive matter adsorbed and repeating the process, it is claimed that thorium-*C* can be obtained in which no thorium-*B* can be detected after the decay of the former. This process is recommended by these authors as a method of separating thorium-*C* in a state of radioactive purity.

In view of the number of recent publications on the determination of acidity in weakly acid solutions, and the marked influence of the hydrogen ion on many reactions, it seemed desirable to investigate more closely this adsorption effect. Careful measurements have been made of the acidity of the solutions used, and of the ratio in which thorium-*B* and thorium-*C* were adsorbed, with a view to determine whether any connexion exists between these two factors.

The ratio of thorium-*B* to thorium-*C* is readily determined from the form of the decay curve. Pure thorium-*C* decays with the period of half change 1 hour, giving out α -rays; pure thorium-*B* shows no initial α -activity, but develops an activity that rises to a

maximum in $3\frac{1}{2}$ hours and then decays with the period of half change 10.6 hours. In a mixture of thorium-B and thorium-C, the amount of -C is proportional to the initial activity, whilst the amount of -B originally present can be calculated from the residual activity after the decay of the original thorium-C, that is, after about six hours.

In the following experiments the activities were measured throughout in the α -ray electroscope and the ratio of thorium-B to -C calculated from the form of the decay curve. The acid used was hydrochloric, a stock solution being diluted to the various strengths required. With a dilute solution of ferric chloride, about 2 grams per litre, it was found that in acid solution hydrolysis took place with precipitation of ferric hydroxide under the following conditions :

Volume of hydrochloric acid used	= 15 to 25 c.c.
Maximum normality of the acid	= $N/20$.
Volume of $N/10$ -fumaric acid solution, or sodium fumarate	= 3 c.c.
Volume of standard ferric chloride	= 3 c.c.

When the whole was raised to boiling, hydrolysis was complete in a few minutes.

In the first series of experiments the active deposit of thorium-B and thorium-C, obtained in the usual way by exposing a negatively charged plate to thorium hydroxide, was dissolved in 15 c.c. of hydrochloric acid each time, the strength of the acid being varied. Solutions of sodium fumarate and ferric chloride were added in the quantities stated above, and the whole boiled to precipitate the iron. The precipitate was washed, quickly dried, and the activity on the filter-paper determined for several hours. The actual decay curves obtained are shown in Fig. 1 along with the dotted curves (a) and (b), which are the theoretical curves for pure thorium-C and for the equilibrium mixture respectively. The scale of activities is so chosen that the initial activity in each case is 100. The results are tabulated below in a somewhat different form, the acidity being expressed as normality of hydrochloric acid used and the ratio given as atoms of thorium-B per atom of thorium-C. In the original active deposit, where the two members were present in radioactive equilibrium, this ratio had the value 10.6.

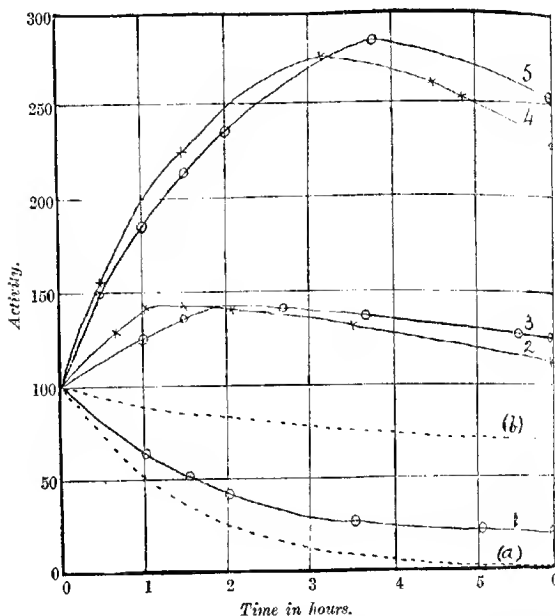
Normality of acid	0.020	0.014	0.007	0.004	0.003
Atomic ratio, Th-B/Th-C.....	3.1	17.7	18.3	33.7	37.7

From these figures it is apparent that, in the most strongly acid solution, thorium-C is adsorbed in considerable excess of the equilibrium ratio, and the decay curve (No. 1) is not very different

from that of pure thorium-*C*. But as the acidity is decreased the relative amount of thorium-*B* increases, until from the most weakly acid solution thorium-*B* is adsorbed in large excess, and the decay curve shows a maximum activity characteristic of thorium-*B*.

It was recognised, however, that in these experiments the normality of the acid as given represents the total hydrochloric acid added, but does not represent the concentration of hydrogen ion after the precipitation. Part of the hydrochloric acid would act

FIG. 1.



on the sodium fumarate to liberate free fumaric acid which, as an organic dibasic acid, would be only slightly ionised. The actual concentration of hydrogen ion would thus be lower than is indicated by the normality. Another and opposing factor is the hydrochloric acid liberated in the solution by the hydrolysis of the ferric chloride. The precipitate of iron contained about 6–10 mg. of ferric oxide, and the amount of hydrochloric acid liberated may readily be calculated as follows:

One gram-molecule, that is, 160 grams, of ferric oxide liberates

six equivalents of hydrochloric acid. If these equivalents are present in 25 c.c., the normality is raised by 240. Thus 10 mg. of ferric oxide raise the normality by 0.015N. This amount is very appreciable in view of the low acidities used.

A second series of experiments was accordingly undertaken in which the actual concentration of hydrogen ion was measured in place of the normality of the hydrochloric acid. The active deposit was dissolved as before in hydrochloric acid of varying strength, fumaric acid and ferric chloride were added, and the iron was precipitated by boiling. The filtrate from each experiment was collected and the concentration of hydrogen ion in it determined by the hydrogen cell. The final acidity thus measured is a complex quantity, being the sum of three factors—the hydrochloric acid used, the fumaric acid added, and the hydrochloric acid liberated by the hydrolysis of the ferric chloride. It is therefore not strictly comparable with the figures in the previous table, which refer only to the normality of the hydrochloric acid used. Indeed, when the active deposit is removed from the plate by simply warming in ferric chloride solution without the addition of any acid, the resulting filtrate is distinctly acid. To reach lower acidities it is necessary to add dilute alkali to the ferric chloride, and care has to be taken to avoid local precipitation of ferric hydroxide during the addition.

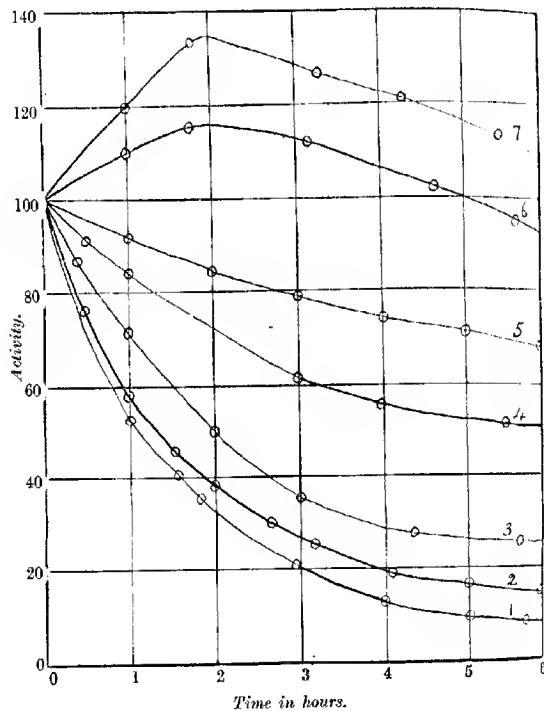
The results of this series of experiments are given in the following table, and the decay curves obtained are shown in Fig. 2.

Final hydron concentration in grams per litre	0.0085	0.0068	0.0063	0.0055	0.0049	0.0046	0.0037
Atomic ratio, Th-B/Th-C	1.2	2.25	3.8	7.8	10.6	13.9	16.9

The same transition from excess of the C-member to excess of the B-member is again evident, and Fig. 3 shows graphically the increase of the ratio Th-B/Th-C with diminishing acidity. The flat portions of the graph can be prolonged at either end, and experimental points have been obtained corresponding with higher and lower acidities than those shown. As the middle part of the graph is the most interesting, it only has been shown on a larger scale than would otherwise be possible. The top portion of this graph is the more difficult to realise experimentally, and in order to control better the lower acidities, an attempt was made to use the buffer mixtures of hydrochloric acid and sodium acetate given by Walpole (T., 1914, 105, 2501, 2521). The active deposit was dissolved in a mixture of hydrochloric acid and sodium acetate having a known hydron concentration, and ferric chloride added

so as to precipitate basic ferric acetate as adsorbent. Unfortunately, with the low concentration of acetic anion in these mixtures and the small quantity of iron permissible as adsorbent, it was not found possible to precipitate basic ferric acetate at an acidity greater than $[H^+] = 10^{-5}$. At this very low acidity thorium-*B* was

FIG. 2.

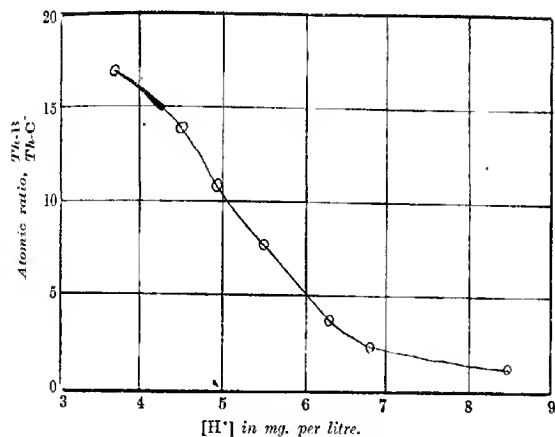


adsorbed in large excess. At the lower end, the curve is limited by the strength of acid in which ferric hydroxide can be formed by hydrolysis. In no experiment was pure thorium-*C* adsorbed, the nearest approach to it being a mixture for which the atomic ratio Th-*B*/Th-*C* was 0.4. It should be noted that even when thorium-*B* and thorium-*C* are present in equal quantity, the decay curve for the mixture differs from that of pure thorium-*C* only very slightly

during the first three hours, and only after four hours does the difference due to the thorium-*B* become really appreciable.

It is worth while comparing the graph of Fig. 3 with that published by von Hevesy (*Phil. Mag.*, 1912, [vi], 23, 628) in his investigation of the electrochemical properties of thorium-*B* and thorium-*C*, in which he deposited both these elements on metallic electrodes at varying potentials. By dipping a noble metal in a solution of one of its salts, for example, silver in silver nitrate, a positive potential was obtained; similarly by dipping such a metal as magnesium or zinc in a solution of its sulphate the electrode took up a negative

FIG. 3.



potential towards the solution. At a positive potential thorium-*C* was deposited on the electrode almost pure, whilst at a sufficiently negative potential thorium-*B* was deposited in large excess; at intermediate potentials the two members were deposited in varying ratios, the proportion of thorium-*C* diminishing as the potential became more negative, and at -0.6 volt against the calomel electrode the two were deposited in radioactive equilibrium. The graph showing the ratio of thorium-*B* to thorium-*C* as ordinate and the electrode potential as abscissa has the same general form as that of Fig. 3, and both curves show an inflexion at the point corresponding with the radioactive equilibrium.

The explanation of this similarity between the curves for electrodeposition and adsorption probably lies in the application of von

Lerch's rule, that the successive products in a disintegration series become more "noble," and in the fact that thorium-*B* and thorium-*C* are known to exist both as colloids and ions. Thorium-*B* exists as a negatively charged colloid and thorium-*C* as a mixture of negative and positive colloid, the amount of positive decreasing with the acidity of the solution. In very weakly acid solution both exist mainly as negative colloids. As the acidity gradually increases, it is suggested that thorium-*B*, as the less noble element, with the greater tendency to form positive ions, passes first into the ionic state, while thorium-*C* remains colloidal. Hence, in the most acid solutions, thorium-*C* is adsorbed almost pure by the positively charged ferric hydroxide, but as the acidity diminishes and thorium-*B* passes into the colloidal state, the latter is adsorbed in increasing ratio and finally in excess of the equilibrium ratio. This reasoning also explains why thorium-*B* cannot be adsorbed in the same high degree of purity as thorium-*C*, for in weak acid that part of the thorium-*C* which is present as negative colloid is adsorbed along with the thorium-*B*.

To test the validity of this colloidal theory a third series of experiments was undertaken in which colloidal ferric hydroxide was used. The active deposit was dissolved as before in 25 c.c. of hydrochloric acid, the strength of which was gradually diminished in successive experiments. Below about $N/10,000$ -acid it is not possible to dilute hydrochloric acid with accuracy, and for these low acidities hydrochloric acid was replaced by mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate, for which the hydrogen-ion concentration is accurately known (see Pridcaux, "Theory and Use of Indicators"). To the solution of the active deposit was added 1 c.c. of ferric hydroxide hydrosol (dialysed free from hydrochloric acid) and the iron was precipitated by addition of a drop of sodium sulphate solution. The precipitated iron carried down thorium-*B* and thorium-*C* in varying proportions, the relative amount of thorium-*B* increasing as before with diminishing acidity. The results are shown in the following table. The acidity of the solutions is given for convenience in the form of $\log [H^+]$; thus, for $N/100$ -acid, $\log [H^+] = -2$.

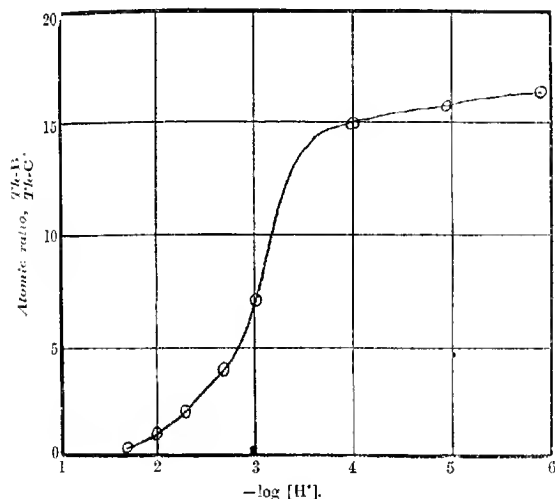
$-\log [H^+]$	1.7	2.0	2.3	2.7	3.0	4.0	4.94	5.91
Atomic ratio, Th-B/Th-C	0.45	0.97	2.0	3.5	7.0	15.0	15.6	16.2

The variation of the ratio of thorium-*B* to -*C* is shown in Fig. 4: the acid end of the curve is limited, of course, by the strength of the acid in which ferric hydroxide can be precipitated. Although not identical with the curve of Fig. 3, this graph shows the same general shape, with a well-defined transition from excess of the

C-member to excess of the B-, and has the same inflexion at the point of radioactive equilibrium.

These results obtained with colloidal iron appear to bear out the colloidal hypothesis previously outlined. Although the concentration of the radioactive matter is insufficient to coagulate the colloidal iron, once this coagulation is effected by addition of a suitable electrolyte the positively charged iron adsorbs that part of the radioactive matter which exists as negative colloid, the electric charges neutralising one other. The inflexion pointed out by von Hevesy and noted again in Figs. 3 and 4 is not so easily

FIG. 4.



explained. Why should these curves, relating to different phenomena, both show an inflexion at the same point, and that the point corresponding with the radioactive equilibrium? One is tempted to look for some connexion between the electrical and colloidal properties of these elements and their atomic stabilities as expressed by their equilibrium ratio.

Further experiments are being carried out in order to obtain more data on this point.

Summary.

1. It has been shown that ferric hydroxide adsorbs thorium-B and thorium-C in proportions varying regularly with the acidity

of the solution. The method is suitable for separating pure thorium-*C* only if the acidity is kept above a certain limit.

2. The variation of the ratio of thorium-*B* and thorium-*C* is continuous, so that the effect seems to be true adsorption and not the formation of a chemical compound between the active matter and the iron.

3. A colloidal theory has been suggested to explain the experimental results; it involves the passage of the radioactive matter from the ionic to the colloidal state, the change being governed by the acidity of the solution.

4. A parallelism has been pointed out between the results reported here and those of von Hevesy for electrode deposition of the same elements. From this parallelism some evidence has been obtained that suggests a connexion between the atomic stabilities of thorium-*B* and thorium-*C* and their electrochemical properties.

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CCXXXV.—*Metallic Derivatives of Nitrophenolic Compounds. Part II. Some Nitrotolyloxides of Metals of Group II.*

By DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD.

IN the present communication, a study has been made of the salts derived from the 1 : 2 : 3-, 1 : 3 : 4-, 1 : 4 : 3-, and 1 : 3 : 6-nitro-cresols, together with some compounds of dinitro-*o*-cresol. By comparing these with the alkaline-earth nitrophenoxides (Goddard, this vol., p. 1161), the change in solubility and in colour due to the influence of the methyl group is dealt with, and since the thalliumdialkyl nitrotolyloxides (Goddard, this vol., p. 1310) resemble the alkali compounds, they have also been alluded to in tracing similarities in solubility. All the substances now described were made by treating the nitrocresols in aqueous solution with the hydroxides or carbonates of the metals. The following hydrated barium salts have now been isolated: the 3-nitro-*o*-tolyloxide (+ 2H₂O); the 4-nitro-*m*-tolyloxide (+ 1H₂O); the 6-nitro-*m*-tolyloxide (+ 6H₂O), together with their anhydrous salts and the anhydrous 3-nitro-*p*-tolyloxide. The anhydrous salts were obtained by heating the hydrated forms at temperatures ranging from 120—160°. In the three cases, where the nitro- and hydroxyl

groups are in the *ortho*-position to one another, the deepest colour is observed, this reaching a maximum in the compound having $\text{CH}_3:\text{OH}:\text{NO}_2 = 1:2:3$. The difference, however, in colour between the compounds containing these groups in positions 1:3:4 and 1:4:3 is not so marked as in the corresponding thalliumdialkyl compounds, and all the salts are darker than barium *o*-nitrophenoxide.

Although the last-named salt has never been obtained with water of crystallisation, it is noticeable that two of the above salts have water of hydration, which may be associated in some way with the presence of the methyl group. Barium 3-nitro-*o*-tolyl-oxide is the most soluble of the three compounds, and more so than barium *o*-nitrophenoxide, but it is much more insoluble than the thalliumdialkyl derivatives. The 6-nitro-*m*-tolyl-oxide having its nitro- and hydroxyl groups in the *para*-position is comparable with barium *p*-nitrophenoxide, and it has almost the same solubility in organic solvents.

In the case of the strontium salts, the following were obtained: the 3-nitro-*o*-tolyl-oxide ($+2\text{H}_2\text{O}$); the 4-nitro-*m*-tolyl-oxide ($+4\text{H}_2\text{O}$); the 3-nitro-*p*-tolyl-oxide ($+4\text{H}_2\text{O}$), and their corresponding anhydrous derivatives, also the anhydrous 6-nitro-*m*-tolyl-oxide. A noticeable feature of the strontium salts is the differently coloured solutions they give when heated with the various solvents, this not being so marked with the barium and calcium compounds. They are more soluble in ethyl acetate than the barium salts, and the greatest solubility is again shown by the derivative of 1:2:3-nitrocresol. When the nitro- and hydroxyl-groups in these compounds are in the *ortho*-position, their colour shows much more of the red and less of the yellow than strontium *o*-nitrophenoxide, and the yellow of the 1:3:6 salts is deeper than that of strontium *p*-nitrophenoxide.

In dealing with nitrophenoxides, it was shown that the calcium compounds usually contain more water of crystallisation than those of barium or strontium, but this has not been found to prevail in the present case. The undermentioned and their anhydrous derivatives are now described: the 3-nitro-*o*-tolyl-oxide ($+2\text{H}_2\text{O}$); the 4-nitro-*m*-tolyl-oxide ($+3\text{H}_2\text{O}$); the 3-nitro-*p*-tolyl-oxide ($+1\text{H}_2\text{O}$); and the 6-nitro-*m*-tolyl-oxide ($+2\text{H}_2\text{O}$). The anhydrous compounds of the first three are differentiated from the barium and strontium analogues by their greater solubility in alcohol, but the 4-nitro-*m*-tolyl-oxide is decidedly the most insoluble in organic solvents. The 6-nitro-compound resembles very closely calcium *p*-nitrophenoxide, being insoluble in most organic media.

Only two magnesium hydrates and their anhydrous salts have been investigated, namely: the 4-nitro-*m*-tolylloxide ($+4\text{H}_2\text{O}$) and the 3-nitro-*p*-tolylloxide ($+3\text{H}_2\text{O}$). These are the most soluble compounds yet described, and their corresponding nitrophenoxides are at present under investigation. Their colour tends more towards orange than is the case with the barium, strontium, and calcium salts. Stadel (*Annalen*, 1883, **217**, 154) describes barium dinitro-*o*-tolylloxide ($+3\text{H}_2\text{O}$), and Cazeneuve (*Bull. Soc. chim.*, 1897, [iii], **17**, 204) a barium salt ($+2\text{H}_2\text{O}$) and also a calcium derivative ($+1\text{H}_2\text{O}$) (*Compt. rend.*, 1897, **124**, 1130), but no investigator seems to have described the strontium salt. It has now been obtained along with its hydrate ($+6\text{H}_2\text{O}$), and is much more soluble than the mononitro-compound and is orange in colour.

Passing to the second vertical series of group II, the colours change from brilliant orange in the magnesium dinitrotolylloxide, through orange-yellow of the zinc salt to brilliant yellow in the cadmium salt. This points to the colour change being due to the metal itself, and not to any acquisition of a quinonoid structure. The following hydrates and their anhydrous derivatives have now been obtained: magnesium dinitro-*o*-tolylloxide ($+3\text{H}_2\text{O}$), the zinc and cadmium salts containing ($+2\text{H}_2\text{O}$) and ($+6\text{H}_2\text{O}$) respectively. Their solubility in organic solvents increases with increasing molecular weight. The solubilities of all compounds have been tested in alcohol, ether, acetone, chloroform, carbon tetrachloride, toluene, light petroleum, ethyl acetate, and pyridine.

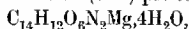
EXPERIMENTAL.

Derivatives of 3-Nitro-o-cresol.— $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}\cdot 2\text{H}_2\text{O}$, bright red needles, which darken in toluene, carbon tetrachloride, or chloroform [Found: N = 5.88 (5.84)*; Ba = 28.70 (28.72); H_2O = 7.62 (7.54) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}$, deep red [Found: N = 6.33 (6.33); Ba = 31.10 (31.07) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}\cdot 2\text{H}_2\text{O}$, orange-red needles, which become deep red in pyridine or alcohol and darken in acetone or ethyl acetate [Found: Sr = 20.93 (20.43); H_2O = 8.47 (8.41) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Sr}$, brownish-red [Found: Sr = 22.87 (22.33) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}\cdot 2\text{H}_2\text{O}$, slender, orange-yellow needles becoming red in chloroform, carbon tetrachloride, or toluene [Found: N = 7.21 (7.36); Ca = 10.57 (10.52); H_2O = 9.54 (9.46) per cent.]. $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ca}$, red [Found: N = 7.97 (8.12); Ca = 11.69 (11.62) per cent.].

Derivatives of 4-Nitro-m-cresol.— $\text{C}_{14}\text{H}_{12}\text{O}_6\text{N}_2\text{Ba}\cdot 1\text{H}_2\text{O}$, red needles

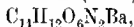
* The figures in the brackets denote the theoretical percentages.

[Found: N = 6.08 (6.08); Ba = 29.71 (29.85); H₂O = 3.82 (3.91) per cent.]. C₁₄H₁₂O₆N₂Ba, deeper red [Found: N = 6.33 (6.33); Ba = 30.89 (31.07) per cent.]. C₁₄H₁₂O₆N₂Sr, 4H₂O, shining, rhomboidal, orange plates, becoming red in carbon tetrachloride or chloroform [Found: Sr = 19.20 (18.86); H₂O = 15.63 (15.51) per cent.]. C₁₄H₁₂O₆N₂Sr, dark red [Found: Sr = 22.76 (22.33) per cent.]. C₁₄H₁₂O₆N₂Ca, 3H₂O, golden-yellow needles darkening in toluene or ethyl acetate [Found: N = 7.04 (7.02); Ca = 10.83 (10.04); H₂O = 12.76 (13.55) per cent.]. C₁₄H₁₂O₆N₂Ca, deep yellow [Found: N = 8.07 (8.12) per cent.].



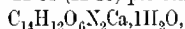
pale orange [Found: Mg = 6.03 (6.06); H₂O = 17.84 (17.96) per cent.]. C₁₄H₁₂O₆N₂Mg, pale orange [Found: Mg = 7.33 (7.41) per cent.].

Derivatives of 6-Nitro-m-cresol.—C₁₁H₁₂O₆N₂Ba, 6H₂O, bright yellow plates, which become deep yellow in carbon tetrachloride, chloroform, or light petroleum [Found: N = 4.93 (4.92); Ba = 24.97 (24.12); H₂O = 19.78 (22.49) per cent.].

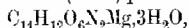


golden-yellow [Found: N = 6.14 (6.33); Ba = 31.10 (31.07) per cent.]. C₁₄H₁₂O₆N₂Sr, bright yellow granules [Found: Sr = 22.28 (22.33) per cent.]. C₁₄H₁₂O₆N₂Ca, 2H₂O, bright yellow granules, which become deep yellow in toluene [Found: Ca = 10.40 (10.52); H₂O = 9.64 (9.46) per cent.]. C₁₁H₁₂O₆N₂Ca, deep yellow [Found: Ca = 11.50 (11.62) per cent.].

Derivatives of 3-Nitro-p-cresol.—C₁₁H₁₂O₆N₂Ba, red shining plates [Found: N = 6.34 (6.33); Ba = 31.27 (31.07) per cent.]. C₁₄H₁₂O₆N₂Sr, 4H₂O, scarlet plates, which become deep red in toluene or chloroform and darken in carbon tetrachloride or light petroleum [Found: N = 6.12 (6.03); Sr = 19.17 (18.86); H₂O = 15.21 (15.51) per cent.]. C₁₄H₁₂O₆N₂Sr, deep red [Found: N = 7.39 (7.14); Sr = 22.61 (22.33) per cent.].



slender, orange-yellow needles, becoming yellow in chloroform and red in toluene [Found: N = 7.79 (7.72); Ca = 11.07 (11.04); H₂O = 4.64 (4.97) per cent.]. C₁₄H₁₂O₆N₂Ca, red [Found: N = 8.16 (8.12); Ca = 11.61 (11.62) per cent.].

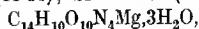


flat, orange needles, which become red in toluene [Found: N = 7.23 (7.32); Mg = 6.77 (6.35); H₂O = 14.08 (14.07) per cent.]. C₁₄H₁₂O₆N₂Mg, red [Found: N = 8.42 (8.51); Mg = 7.39 (7.41) per cent.].

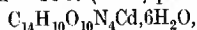
Derivatives of Dinistro-o-cresol.—C₁₄H₁₀O₁₀N₄Sr, 6H₂O, brilliant yellow needles, becoming orange in ether or chloroform and darken-

2048 HIGSON : REACTION BETWEEN PERSULPHATES AND SILVER.

ing in toluene [Found: N = 9.56 (9.49); Sr = 14.67 (14.84); H₂O = 17.82 (18.31) per cent.]. C₁₄H₁₀O₁₀N₄Sr, deep orange [Found: N = 11.70 (11.61); Sr = 17.90 (18.17) per cent.].



golden-yellow needles, becoming orange in carbon tetrachloride or toluene [Found: Mg = 5.11 (5.14); H₂O = 11.65 (11.42) per cent.]. C₁₄H₁₀O₁₀N₄Mg, brilliant orange [Found: Mg = 5.78 (5.81) per cent.]. C₁₄H₁₀O₁₀N₄Zn, orange-yellow granules [Found: N = 11.42 (11.29); Zn = 13.55 (13.17); H₂O = 7.29 (7.26) per cent.]. C₁₄H₁₀O₁₀N₄Zn, orange-yellow [Found: N = 12.39 (12.18); Zn = 14.60 (14.21) per cent.].



brilliant yellow plates, becoming orange in toluene or chloroform [Found: Cd = 18.30 (18.27); H₂O = 17.82 (17.57) per cent.]. C₁₄H₁₀O₁₀N₄Cd, orange yellow [Found: Cd = 21.75 (22.16) per cent.].

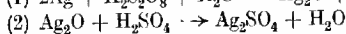
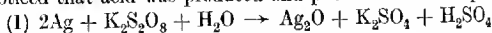
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[Received, October 6th, 1921.]

CCXXXVI.—The Reaction between Persulphates and Silver.

By GEOFFREY ISHERWOOD HIGSON.

THE action of solutions of persulphates on metallic silver was first noticed by Marshall (*J. Soc. Chem. Ind.*, 1897, **16**, 396), who found that the silver gradually went into solution and that at the same time a black deposit was formed, which he considered was a peroxide, Ag₂O. The reaction was further investigated by Levi, Migliorini, and Ercolini (*Gazzetta*, 1908, **38**, i, 583), who noticed that acid was produced and put forward the equations:



as representing the course of the reaction. The solution might thus remain neutral or become acid, according to the relative velocities of the reactions (1) and (2). By the action of persulphates upon silver nitrate solution, Marshall (*Proc. Roy. Soc. Edin.*, 1900, **23**, 168) obtained a similar black precipitate, which he considered was the same peroxide, but Austin (*T.*, 1911, **99**, 262) concluded, on account of its high sulphate content, that it was a mixture of silver peroxide and silver persulphate, whilst Tarugi (*Gazzetta*,

1902, 32, ii, 383) considered it to be the silver salt of Caro's acid, namely, Ag_2SO_5 .

There is some doubt as to the composition of silver peroxides, which are usually obtained, mixed or combined with salts, as anodic deposits in the electrolysis of solutions of silver salts in a divided cell. For example, by the use of silver nitrate solution a black, crystalline powder of metallic appearance is obtained (Ritter, *Gehlen's neues J.*, 1804, 3, 561), which, on washing, immediately commences losing oxygen, silver nitrate being set free and passing into solution. The undecomposed crystals have the empirical formula $\text{Ag}_7\text{O}_{11}\text{N}$ (Sule, *Zeitsch. anorg. Chem.*, 1896, 12, 89; Tanatar, *ibid.*, 1901, 28, 331) and later work has shown that they are very probably a double compound corresponding with the formula $\text{AgNO}_3 \cdot 2\text{Ag}_2\text{O}_4$ (Babarovský and Kužma, *Zeitsch. physikal. Chem.*, 1909, 67, 48; Brown, *J. Physical Chem.*, 1916, 20, 680). Since oxygen is lost during the washing, the original peroxide may, however, contain a higher proportion of oxygen; on the other hand, from the anodic decomposition curves of both nitrate and sulphate solutions, Bose (*Zeitsch. anorg. Chem.*, 1905, 44, 237) concluded that the oxide was Ag_2O_2 .

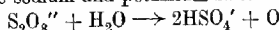
In opposition to the view that these substances are double compounds of a peroxide of silver and ordinary silver salt—the peroxides are never obtained pure by this method—Watson (T., 1906, 89, 578) concluded that the black silver deposit $\text{Ag}_7\text{O}_{11}\text{N}$ was a "peroxynitrate," that is, a definite compound, since he obtained it under varying conditions. He found that, on boiling, the dioxide, Ag_2O_2 , was formed, and he described the properties of this and verified its composition.

In the course of some experiments on the action of persulphates on the photographic negative, it was necessary to investigate the action of persulphate on silver, both in the metallic and the ionic form, and it has been found that sodium or potassium persulphate solution converts metallic silver into a peroxide containing a greater proportion of oxygen than corresponds with the formula Ag_2O_2 , whilst the acidity of the solution at the same time increases. When a strong (20 per cent.) solution of the sodium salt is used, the peroxide can rapidly be obtained in quantity, but owing to the much smaller solubility of the potassium salt the reaction with this is much slower (for example, eighteen hours) and the yield much lower, for the peroxide is unstable and decomposes continuously from the time of its formation. With the ammonium salt, no peroxide is formed, but the ammonium radicle is oxidised to nitric acid (compare Marshall and Ingless, *Proc. Roy. Soc. Edin.*, 1902, 24, 88). When the reaction is continued for more than about

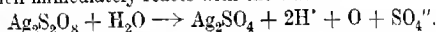
one hour, the product is contaminated with sulphate, which is always present to a slight extent.

It has been found that the same peroxide is produced when persulphates react with silver nitrate, again with increase in acidity, but in this case the contamination with silver sulphate is greater.

An explanation of this contamination has been found in the catalytic decomposition of persulphates by silver ions, previously noticed by Marshall in the case of the ammonium salt, whereby in the case of the sodium and potassium salts the reaction



is immensely accelerated. The HSO_4' ions thus formed react continuously with silver ions, and as these are present in much greater quantity when silver nitrate is used, the amount of silver sulphate formed is consequently greater in this case. Moreover, the catalytic effect increases with increase of concentration of the silver ions, and this again tends to produce more contamination when silver nitrate is used in the preparation. A possible explanation of this catalytic effect is the intermediate formation of silver persulphate, which then immediately reacts with the water:



As might be expected, it has been found that the presence of an oxidisable substance, such as gelatin, prevents the formation of peroxide, whilst it is itself oxidised; but it does not prevent the catalytic decomposition of the persulphate, with formation of acid sulphate. The application of this result to the action of persulphate as a photographic reducer is obvious, and will be discussed in another place.

EXPERIMENTAL.

Preparation of the Peroxide from Sodium Persulphate.

Metallic silver was obtained in the finely divided, crystalline form by precipitation from silver nitrate with metallic magnesium (compare Dodgson, *Phot. Jour.*, 1911, 51, 265). The excess of magnesium was removed with dilute sulphuric acid, and the silver, which was of a grey colour, and in the form of crystals about 0.001 mm. in length, thoroughly washed by decantation. About 3 grams of this were introduced, wet, into a solution in 100 c.c. of water of 20 grams of sodium persulphate. This was the purest commercial product, but was considerably contaminated with acid sulphate, due to decomposition. It was not purified—a difficult matter—since acid sulphate is rapidly formed again during the reaction. The mixture was then stirred mechanically. It almost immediately darkened and after half an hour the grey silver

appeared to have been converted into a black powder, whilst at the same time the acidity of the mixture increased. It was found that the solid consisted of a peroxide, with a considerable amount of unconverted silver, which usually persisted after the reaction had continued for an hour or more. Since the sulphate content rises with increase of time of reaction, the product, when free from silver, was contaminated with silver sulphate. It was washed with dilute sulphuric acid and water, and obtained as a black, metallic-looking powder, which, after drying on a porous tile over calcium chloride, lost its metallic appearance and finally resembled manganese dioxide. It decomposed continuously from the time of its formation, whether wet or dry, losing oxygen and becoming alkaline owing to the formation of silver oxide.

The substance thus obtained exhibits all the properties of the dioxide described by Watson; for example, it gives deeply coloured solutions with concentrated nitric acid or concentrated sulphuric acid, which decompose with loss of colour, gradually at the ordinary temperature, and rapidly on heating. It is, as might be expected, a strong oxidising agent; for example, it liberates iodine from acidified potassium iodide and converts quinol in acid solution into *p*-benzoquinone.

The same procedure was carried out in 5 per cent. gelatin solution. No peroxide was formed, although the silver gradually dissolved and the solution became strongly acid.

Analysis of the Product.

From numerous analyses it became evident that the more rapidly the product was removed from the filter and analysed, the higher was the percentage of the available oxygen. Since a period of a few minutes is sufficient substantially to alter the amount of oxygen, it seems that the analyses by Austin and by Watson (*loc. cit.*) of the dried products are of doubtful value.

To ascertain, if possible, towards what limit this available oxygen tended, experiments were made in which the washing of the product was carried out with ice-cold acid and water, in order to retard the decomposition. No evolution of gas was apparent under these conditions, but the procedure does not avoid decomposition during the formation of the peroxide, which cannot conveniently be carried out at 0° owing to the slowness of reaction at this temperature.

The analyses were made according to the method of Babarovský and Kužma (*loc. cit.*), the product being thrown wet into a known quantity of *N*/10-oxalic acid and an excess of 2*N*-sulphuric acid, and rapidly stirred to promote reaction with the oxalic acid, which

was oxidised to carbon dioxide. Solution was completed by heating to boiling and the excess of oxalic acid estimated by titration with permanganate. The slight excess of this was then removed by oxalic acid, and after cooling, the silver estimated by Volhard's thiocyanate method.

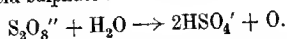
Results of Analyses.—The ratio is that of atoms of total oxygen to atoms of silver, that is, it would be 1 for Ag_2O_2 , and 1.33 for Ag_3O_4 .

Preparation.	Time of keeping. (days).	Conditions.	Ratio.
No. 62	6	Exposed to air.	0.777
		Kept over CaCl_2 .	0.735
	11	" " "	0.718
No. 63	0	Taken wet from the filter.	1.047
	"	" " "	1.044
	"	" " "	1.033
	1	Kept over CaCl_2 .	0.965
No. 66	0	Washed at 0° and taken wet from the filter.	1.245
			1.251
			1.185
No. 70	"	" " "	1.29
			1.29

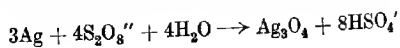
These results show that the undecomposed peroxide contains more oxygen than corresponds with the formula Ag_2O_2 , but on no occasion was quite sufficient oxygen obtained to justify the formula Ag_3O_4 .

Mechanism of the Reaction.

The explanation of Levi, Migliorini, and Ercolini, that the increase of acidity is due to the formation of sulphuric acid and undissolved silver oxide simultaneously, is obviously unsatisfactory; the acidity must arise from the decomposition of water during the reaction, the oxygen going to form the silver peroxide, while the hydrogen gives acid sulphate:



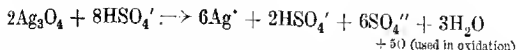
It should therefore be possible to trace the course of the reaction by determining the ratio between the increase of acidity and the quantity of silver converted into peroxide. Unfortunately, oxygen is invariably evolved during the reaction, either from actual decomposition of peroxide already formed, or directly from the reaction between the persulphate and water, this reaction being, as will be shown below, catalysed by silver ions, and this method is useless. If the peroxide has the formula Ag_3O_4 , the reaction must be of the form



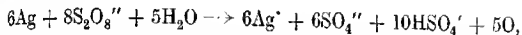
and the increase of acidity is considerable in comparison with the silver dissolved.

When an oxidisable substance is present, the peroxide apparently reacts with this at once, for the silver goes into solution without any production of black peroxide, as may easily be demonstrated by mixing the persulphate solution with a gelatin solution containing colloidal silver.

This requires a reaction of the form



and therefore the complete reaction for the solution of silver in persulphate when an oxidisable substance is present must be of the form



a reaction considerably more complex than any that has been previously proposed, and further complicated by the fact that the persulphate ion alone may react directly with the water.

Preparation of the Peroxide from Silver Nitrate.

Sodium persulphate, although invariably contaminated with acid sulphate, gave much better results than the slightly soluble potassium salt used by Austin, since the more dilute solutions favoured decomposition.

Ten grams of silver nitrate dissolved in 10 c.c. of water, and 8 grams of sodium persulphate in 60 c.c. of water, were cooled to 0° , and the solutions rapidly mixed, the mixture being kept cold in ice. There was an immediate, grey precipitate formed, which was collected at once in a Gooch crucible, and on analysis was found to consist of almost pure silver sulphate containing only a slight trace of available oxygen. The filtrate, on keeping at 0° , commenced to throw down a black precipitate in less than five minutes; after fifteen minutes the precipitation appeared to be complete, and the product was collected, washed with ice-cold water, and analysed immediately. It was found to contain a large percentage of sulphate; but otherwise exhibited all the reactions of the peroxide, and appeared to be a mixture of silver peroxide and silver sulphate.

Analysis of the Product.

The analysis was carried out on two separate portions. In one portion the ratio of available oxygen to silver was obtained as described above, and in the other portion the ratio of sulphate to

silver was determined by decomposing the product with hydrochloric acid, removing the silver as chloride, and estimating the sulphate in the filtrate as barium sulphate. From these two ratios it is possible to calculate the value of x when the formula is expressed as $\text{Ag}_2\text{SO}_4(\text{AgO}_x)_n$, that is, the formula of the admixed peroxide.

Preparation No. 79.—The peroxide-sulphate mixture was prepared at 0° as described above, and washed four times with water at 0° . Two determinations were made of the ratio of available oxygen to silver, the mean being taken, and one of sulphate to silver. Formula calculated: $\text{Ag}_2\text{SO}_4(\text{AgO}_{1.265})_{1.654}$, that is, the product is a mixture of 1 part of silver sulphate with 1.654 parts of a peroxide containing slightly less oxygen than corresponds with the formula Ag_3O_4 .

A similar determination of another preparation gave the result $\text{Ag}_2\text{SO}_4(\text{AgO}_{1.237})_{1.59}$, and there seems to be little doubt that the precipitate is a mixture of peroxide and sulphate.

Catalysis by Silver Ions of the Decomposition of Persulphates.

From experiments with mixtures of solutions of silver nitrate and of neutral sodium or potassium persulphate it was found that the acidity increased continuously from the time of mixing. It was therefore obvious that the decomposition of persulphates in solution, namely, $\text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + \text{O}$, is catalysed by the silver ions, since this decomposition takes place only very slowly at the ordinary temperature with neutral solutions (Green and Masson, T., 1910, 97, 2083). The extent of this catalysis was determined for potassium persulphate, which is the most convenient salt to obtain pure.

A $N/20$ -solution of potassium persulphate, with additions of silver nitrate, was maintained at 18° and estimations made of the acidity of portions removed at known intervals after the addition of the silver. To render the acidimetry possible without formation of silver oxide, the solution to be tested was run into an amount of sodium chloride solution rather greater than that necessary to convert all the silver into silver chloride.

Since the reaction can be only approximately monomolecular owing to the side reaction with the silver, the values of $\frac{1}{t} \log_e \frac{a}{a-x} = k$, the velocity constant, were found to be somewhat irregular, but when the formula $k = \frac{1}{t - t_1} \log_e \frac{a - x_1}{a - x}$ was employed, where t_1 was about five minutes, the constancy was reason-

ably good, errors due to the side reaction being eliminated, as the following results for $N/250$ -concentration of silver nitrate indicate. Temperature 18° ; a , the original concentration of persulphate expressed as c.c. of standard alkali, is 24.25.

t in mins.	x = c.c. of alkali required for neutralisation.	$k = \frac{1}{t - \frac{1}{2}} \log \frac{a - 0.2}{a - x}$
2	0.05	—
6	0.2	—
11	0.3	0.0008
30	0.8	0.0010
60	1.3	0.00085
90	1.7	0.00077
150	2.4	0.00068
195	3.05	0.00067
		Mean 0.00079

The results of this and similar experiments are as follows :
Temperature 18° . Concentration of potassium persulphate = $N/20$.
 c = concentration of silver nitrate.

c .	k .	k/c .
$N/250$	0.00079	0.20
$N/100$	0.0021	0.21
$N/50$	0.00375	0.19

These results show that the catalysed decomposition of the persulphate is an approximately monomolecular reaction, and that the velocity of decomposition is approximately proportional to the concentration of the silver ion.

The author desires to express his thanks to Dr. Slater Price for the interest he has taken in this work, and for his valuable advice and criticism.

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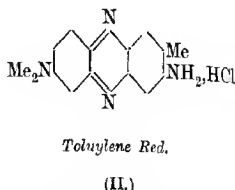
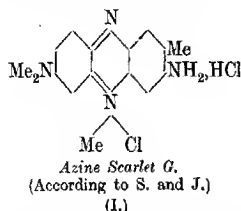
[Received, October 20th, 1921.]

CCXXXVII.—*Structure and Colour of the Azine Scarlets.*

By JULIUS BEREND COHEN and HERBERT GRACE CRABTREE.

IN connexion with an inquiry into the antiseptic action of certain dyestuffs undertaken for the Medical Research Council, it was found necessary to examine specimens of Azine Scarlets which resemble in structure the yellow dye acriflavine, well known as an antiseptic. In Green's edition of "Organic Colouring Matters" by Schultz and Julius (1904) it is stated on p. 228, under No. 582, that Azine Scarlet G (the only one mentioned) is obtained by the action of

nitrosodimethylaniline on *m*-aminodimethyl-*p*-toluidine, and has the following formula (I) :

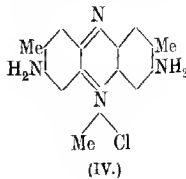
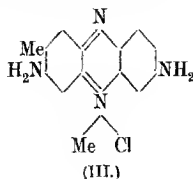


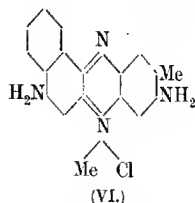
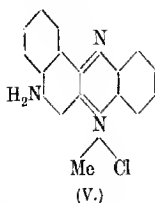
According to this formula, Azine Scarlet G appears as the methochloride of Toluylene Red (II).

If, however, the preparation is carried out according to the directions given under a patent by Meister, Lucius, & Brünig, No. 69188, or if Toluylene Red is converted into the methochloride, the same colouring matter is apparently formed; but instead of the scarlet dye known commercially as Azine Scarlet G, a substance is produced in both cases which has a bright magenta colour.

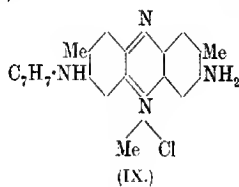
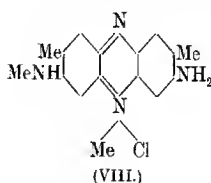
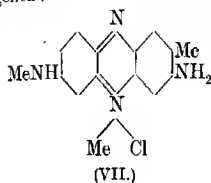
In the patent literature on the subject there are several methods given for preparing scarlet dyes of the phenazine group. Thus, Friedländer ("Fortschritte der Teerfarbenfabrikation," Vol. IV, p. 376) mentions a patent, No. 80758 by Meister, Lucius, & Brünig "for preparing red basic azine dyes" from nitroso-mono- or -di-methyl-*o*-toluidine, nitroso-mono- or -di-ethyl-*o*-toluidine, and *m*-aminodimethyl-*p*-toluidine, and in the same volume (p. 380) there is a further patent, No. 86608, by the Farbwerke Mühlheim, "for preparing scarlet dyes of the safranine group" by heating *p*-aminoazo-compounds with *o*-aminodimethyl-*p*-toluidine. A number of these compounds have now been prepared, from which it appears that the substitution of methyl and other radicles for hydrogen in the amino-group produces a change of tint from scarlet to magenta—in other words, the introduction of the heavier auxochrome group causes a displacement of tint towards the blue end of the spectrum.

Thus, the following series of aminophenazine salts of the methochlorides have a scarlet colour :

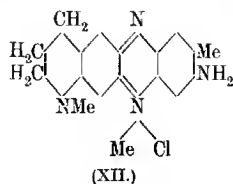
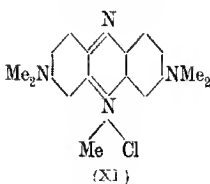
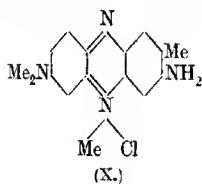




The following have a bluer tint intermediate between scarlet and magenta :

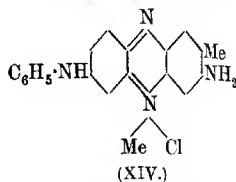
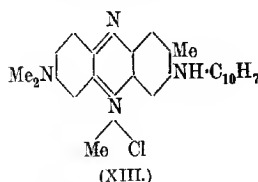


Whereas the following three compounds have a magenta or bluish-red tint.



Further examples of the shifting of tint towards the blue by the introduction of heavier radicles into the amino-group are illustrated

by the dye described under D.R.-P. 89659 by Meister, Lucius, & Brünig (Friedländer, *op. cit.*, Vol. IV, p. 379), which has probably the following formula (XIII); it dissolves in water with



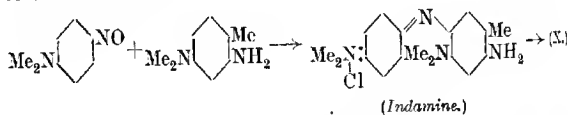
a bluish-violet and in alcohol with a reddish-violet colour; and by the dyestuff (XIV) described in D.R.-P. 85231 (Friedländer, *op. cit.*, Vol. IV, p. 377), which dissolves with a violet colour.

The same shifting of tint towards the blue is observed in rosaniline and in its methyl and phenyl derivatives, which show a similar gradation from magenta to violet and blue by the introduction of heavier radicles into the amino-group.

EXPERIMENTAL.

3-Amino-7-dimethylamino-2-methylphenazine Methochloride.

The colouring matter described in Green's edition of "Organic Colouring Matters" by Schultz and Julius (1904) as Azine Scarlet G (formula X) has been prepared by three methods. (1) One method (given by Schultz and Julius) is that described in D.R.P. 69188 (Friedländer, *op. cit.*, Vol. III, p. 397) by the action of nitrosodimethylaniline upon 2-aminodimethyl-*p*-toluidine according to the reaction:



It will be seen that in passing from the indamine to the final stage a methyl group is eliminated from the dimethylamino-group.

The 2-aminodimethyl-*p*-toluidine was obtained by the nitration of dimethyl-*p*-toluidine and subsequent reduction with stannous chloride and hydrochloric acid. The latter, recrystallised from light petroleum, formed large prisms, m. p. 53°.

Fifteen parts of the base were dissolved in 100 parts of 50 per cent. acetic acid, and 18.6 parts of *p*-nitrosodimethylaniline hydrochloride added. A transient green coloration due to the formation of the intermediate indamine was immediately succeeded, on warm-

ing on the water-bath, by a deep blue, which changed to magenta after two or three hours' heating. The whole was diluted with 200 parts of water, filtered hot, and the colouring matter precipitated with sodium chloride and zinc chloride.

(2) The second method consisted in converting Toluylene-red into the methochloride. The red dye was prepared according to Witt's method (*Ber.*, 1879, 12, 931) by mixing 3.6 grams of *p*-nitrosodimethylaniline hydrochloride with 2.4 grams of *m*-tolylene-diamine, each dissolved in 50 c.c. of water at 30°, and allowing the mixture to stand over-night. The dark green indamine was filtered, pressed, dissolved in 100 c.c. of water, and boiled for three hours, when a drop on filter-paper gave only a faint blue rim. The solution was filtered and the dye salted out. When recrystallised from alcohol, it formed a brown, microcrystalline powder.

The colouring matter was acetylated by heating 5 grams with 15–20 grams of acetic anhydride and 2–3 grams of fused sodium acetate: having been poured into water, the acetyl derivative was precipitated with sodium hydroxide, filtered, and crystallised from alcohol. It formed brown plates. Two grams of the acetyl derivative were dissolved in 5 grams of nitrobenzene heated at 170° and 0.9 gram of methyl sulphate was added. The heating was continued for a minute and the product cooled. The brownish-black solid which separated was filtered, washed with ether, dried, and boiled with 10 c.c. of concentrated hydrochloric acid for half an hour. A deep blue solution was formed, which was poured into water, when the colour changed to bright magenta. The methochloride was salted out and formed a semi-solid, iridescent, green mass, which after drying became hard and when crystallised from a mixture of benzene and alcohol formed a microcrystalline powder with a dark green lustre (Found: $N = 17.0$. $C_{15}H_{20}N_4Cl_2$ requires $N = 16.5$ per cent.).

The products obtained by the two methods gave identical colour reactions with alkalis and acids, as described in the patent (*loc. cit.*).

According to the first method, the change from indamine to the final stage takes place with the elimination of a methyl group from the dimethylamino-group.

(3) In order to obtain further evidence on this point, a third method was adopted for preparing the colouring matter, namely, from nitrosodimethylaniline hydrochloride and the 2-aminomonomethyl-*p*-toluidine, in which case hydrogen would be eliminated in place of a methyl group. Monomethyl-*p*-toluidine was prepared by Ullmann's method (*Annalen*, 1903, 327, 165). One hundred and thirty grams of *p*-toluidine were dissolved in 180 c.c. of ether in a flask provided with a reflux condenser, and 99 grams of methyl

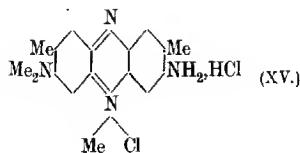
sulphate were run in during ten minutes. Heat was developed and the flask was cooled with water. The methosulphate, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{HSO}_4$, rapidly formed and in a short time the contents of the flask became nearly solid. Water was added, the ether layer separated, and the aqueous layer further extracted. The ether was removed without dehydrating and the crude base purified by conversion into the nitroso-derivative and subsequent reduction. The crude base was dissolved in 150 c.c. of concentrated hydrochloric acid and 500 c.c. of water, cooled to $0-5^\circ$, and a solution of 45 grams of sodium nitrite slowly run in. A nearly colourless nitrosomethyl-*p*-toluidine separated and was filtered, washed with water, and dried on a porous plate. The product (42 grams; m. p. 53°) was dissolved in a minimum quantity of alcohol and a solution of 130 grams of stannous chloride in 200 c.c. of concentrated hydrochloric acid added gradually with shaking. After heating on the water-bath for half an hour, the whole was made alkaline and distilled in steam. Sodium chloride was added to the distillate and the base extracted with ether. The ether solution was dehydrated over potassium hydroxide and the ether removed. The residue distilled at 200° . The yield was 16 grams, or 48 per cent. of the theoretical. The nitration of the base was carried out as described by Pinnow (*Ber.*, 1895, **28**, 3040). The yield was theoretical. The substance crystallises in large, red prisms, m. p. 59° . The reduction was effected with stannous chloride. Thirty-one grams of stannous chloride were dissolved in 50 c.c. of concentrated hydrochloric acid and 5 grams of the nitro-base added slowly. Rapid reduction and decolorisation of the substance took place, after which the mixture was heated for half an hour on the water-bath. The solution was then made alkaline and the base extracted with ether. The ether extract was dehydrated and the ether removed. The 2-aminomonomethyl-*p*-toluidine remained as a pale brown oil, which was used without further purification. A mixture of 3.4 grams of the base, 4.6 grams of *p*-nitrosodimethyl-aniline hydrochloride, and 25 grams of 50 per cent. acetic acid was heated on the water-bath for three hours until a sample diluted with water and dropped on filter-paper gave only the faintest suggestion of blue on the rim of the spot. It was then diluted, filtered, and the colouring matter salted out with sodium and zinc chlorides. The product appeared to be identical in every respect with those prepared by the two previous methods.

3-Amino-7-dimethylamino-2:8-dimethylphenazine Methochloride.

The *p*-dimethylamino-*o*-toluidine required was obtained by coupling dimethyl-*o*-toluidine with diazotised sulphanilic acid, a

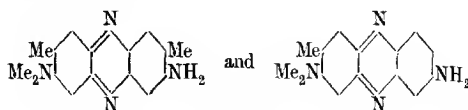
process which is effected exactly as in the preparation of methyl-orange, except that the operation is conducted at room temperature. Dimethyl-*o*-toluidine (1 mol.) is exactly neutralised with hydrochloric acid diluted with about four times its weight of water. Sulphanilic acid (1 mol.) is dissolved in an equivalent of sodium carbonate solution (15 parts of water to 1 part of sulphanilic acid), and sodium nitrite (1 mol.) dissolved in water added, the whole being acidified with hydrochloric acid (2.1 mols.). The hydrochloride of the base in solution having been added to the diazo-solution, the mixture is made slightly alkaline with a few c.c. of sodium hydroxide solution and stirred for four hours, when the colouring matter is thrown down in orange leaflets. It is filtered, washed with concentrated brine, and dried at 50°. It was reduced by adding to the substance dissolved in an excess of boiling hydrochloric acid zinc dust until completely decolorised. It was then cooled, filtered, neutralised with sodium hydroxide, and the base extracted with ether. The ether extract was dehydrated with potassium hydroxide and the ether removed. A pale brown oil remained which soon solidified, and was used without further purification. The same substance is described by Bernthsen (*Ber.*, 1892, **25**, 3128), who obtained it by nitrating *o*-toluidine, methylating the product, and finally reducing the nitro-group, but the above method was found to be much more convenient and more easily carried out.

Sixteen parts of *p*-dimethylamino-*o*-toluidine and 15 parts of 6-dimethylamino-*m*-toluidine were dissolved in 300 parts of water, 20 parts of concentrated hydrochloric acid, and 30 parts of 50 per cent. acetic acid, and cooled to 10° with stirring. Thirty parts of sodium dichromate in 400 parts of water were run in during three hours. A bluish-red coloration developed immediately and became more intense as the oxidising agent was added. The mixture was finally warmed on the water-bath for an hour, filtered, and salted out with zinc chloride and sodium chloride. The product was purified by solution in water, filtration, and reprecipitation with salt solution. It could not be recrystallised from alcohol or dilute hydrochloric acid. The substance, by analogy with the formation of tetramethyldiaminophenazine (p. 2064), has the following structure :



It dissolves in water with a magenta colour similar to that of Toluylene-red methochloride.

Attempts to prepare



by condensing by the above reaction the *p*-diamine with *m*-phenylene- and *m*-tolylene-diamine were unsuccessful. With tolylene-diamine, a dark brown coloration rapidly developed and assumed a dirty red colour at a later stage, a mass of sticky, dark brown crystals being deposited, which could not be purified.

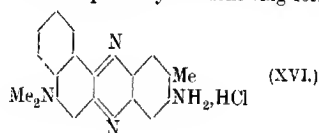
5-Aminonaphthaphenazine 7-Methochloride (Formula V).

This substance was prepared according to the method described by O. Fischer and Hepp (*Ber.*, 1890, **23**, 845) by heating in a sealed tube for five to six hours at 160° *o*-phenylenediamine (1 mol.) and benzenazo- α -naphthylamine hydrochloride (1 mol.) with 10 parts of alcohol. On cooling, dark red crystals separated. They were filtered and crystallised from alcohol containing hydrochloric acid. The substance obtained in this way is the hydrochloride of aminonaphthaphenazine. It forms dark red crystals which are slightly soluble in water, but on heating are hydrolysed and the base is precipitated. The acetyl derivative was obtained by heating the base with acetic anhydride and fused sodium acetate. On cooling, the acetyl derivative crystallised. It was heated at 160° with ten to twenty times its weight of nitrobenzene and the equivalent of 1 molecule of methyl sulphate added. On standing, crystals of the methosulphate separated. They were filtered, washed with ether, and heated with concentrated hydrochloric acid, when the methochloride slowly crystallised in dull red, microscopic crystals. The substance dissolves in water with a bright scarlet colour like the hydrochloride, C₁₇H₁₄N₃Cl.HCl, but is not so readily hydrolysed as the latter.

9-Amino-5-dimethylamino-10-methylnaphthaphenazine Hydrochloride.

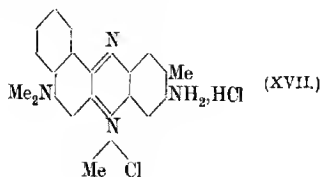
The 4-nitrosodimethyl- α -naphthylamine hydrochloride required in this preparation is described by Friedländer and Welms (*Ber.*, 1888, **21**, 3123). The reaction goes smoothly and the yields of both base and nitroso-derivative are nearly theoretical. The latter is less soluble than the corresponding nitrosodimethylaniline, and

therefore it is difficult to isolate the intermediate indamine in aqueous solution. 2.3 Grams of nitrosodimethylnaphthylamine hydrochloride were dissolved in 20 c.c. of hot glacial acetic acid, to the solution 1.2 grams of *m*-tolylenediamine dissolved in 20 c.c. of 50 per cent. acetic acid and 1 c.c. of concentrated hydrochloric acid were added, and the mixture was heated on the water-bath for four hours. A magenta colour developed rapidly, losing its blue tint on continuous heating and becoming more crimson in shade. The solution was finally boiled, diluted with 100 c.c. of water, filtered, and the hydrochloride of the dye precipitated with brine. It was purified by redissolving it in water and reprecipitating with brine. A considerable amount of by-product was formed during the reaction, which was still more noticeable when *m*-phenylenediamine was used in place of the tolylenediamine. The colouring matter prepared as described is not very soluble in water, but dissolves in alcohol. It forms a black, shining powder which dissolves in water with a magenta colour similar to that of Toluylene-red methochloride. It has probably the following formula :



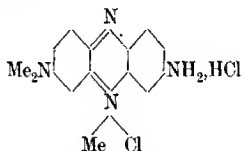
9-Amino-5-dimethylamino-10-methylnaphthaphenazine Methochloride.

The process was conducted as described above, but the *m*-tolylene-diamine was replaced by *p*-dimethylamino-*o*-toluidine. 2.4 Grams of 4-nitrosodimethyl- α -naphthylamine hydrochloride, dissolved in 20 c.c. of glacial acetic acid, were added to 1.5 grams of the dimethylamino-*o*-toluidine in 20 c.c. of 50 per cent. acetic acid and 1 c.c. of concentrated hydrochloric acid. A bright crimson colour developed rapidly, and after three hours' heating on the water-bath the dye was separated and purified as in the previous case. The hydrochloride of this colouring matter is even less soluble than the above hydrochloride, but is readily soluble in alcohol. The formula may be represented as follows :

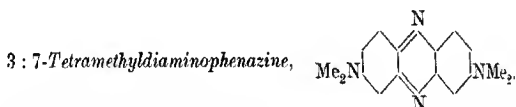


3-Amino-7-dimethylaminophenazine Methochloride.

This compound, which has been described by Karrer (*Ber.*, 1916, 49, 1643; 1917, 50, 420), was prepared in order to compare the effect on the colour caused by the absence of methyl groups in the nucleus of the two benzene rings. It was obtained by oxidising a mixture of dimethyl-*p*- and -*m*-phenylenediamine with potassium dichromate. The phenazine salt was salted out by zinc and sodium chlorides, from which the base was precipitated by the addition of sodium hydroxide or ammonia. It dissolves in alcohol and in dilute acid with a deep violet colour.



It is the methochloride of "Neutral-violet," which has a similar tint. The absence of methyl groups in the nucleus seems to produce an effect similar to that obtained by methylating the amino-group, although it is curious that the tetramethyldiaminophenazine about to be described should have a redder tint in spite of the absence of methyl groups in the nucleus.



This substance is described by Karrer (*Ber.*, 1916, 49, 1643) as being formed by oxidising a mixture of dimethyl-*p*-phenylenediamine and dimethyl-*m*-phenylenediamine with potassium dichromate solution in presence of hydrochloric acid. The process was carried out as described and the phenazine compound separated in the form of the hydriodide, from which the base was precipitated by ammonia, filtered, washed, and extracted with alcohol. The residue was dissolved in dilute hydrochloric acid and the hydrochloride evaporated to dryness in a vacuum desiccator. The methochloride was prepared in the usual way (see p. 2059) by the action of methyl sulphate on the acetylated base dissolved in nitrobenzene and subsequent hydrolysis with concentrated hydrochloric acid. The colour of the methochloride dissolved in water, which closely resembles that of the hydrochloride (as is usually the case), is a

violet-red, as described by Karrer. According to Karrer, the base has the formula given above.

Bamberger (*Annalen*, 1890, **257**, 1) has shown that *N*-methyltetrahydroquinoline (kairolin) has properties closely resembling those of dimethylaniline, and, like the latter, yields a nitroso-derivative. It seemed an interesting point to determine whether an azine colouring matter is produced in the same way as Toluylene-red methochloride and also to examine the colour of the product.

*3-Amino-2-methyl-N-methyltetrahydroquinolinophenazine
Methochloride (Formula XII).*

The tetrahydroquinoline and its *N*-methyl derivative were prepared by the method of Hoffmann and Königs (*Ber.*, 1883, **16**, 728) and the latter was converted into the nitroso-compound (Königs and Freer, *Ber.*, 1885, **18**, 2388). A mixture of 2.6 grams of nitroso-*N*-methyltetrahydroquinoline, 1.5 grams of *p*-dimethylamino-*o*-toluidine, 15 c.c. of glacial acetic acid, and 2 c.c. of concentrated hydrochloric acid was warmed gently on the water-bath. Heat was developed and the liquid acquired a brilliant green colour which rapidly changed through brownish-black, dull scarlet, to magenta. The heating was continued for three to four hours, when the product was dissolved in 50 c.c. of hot water, filtered, and the colouring matter precipitated with zinc chloride and brine. It formed a green, iridescent mass, which was at first sticky, but rapidly hardened. The substance dissolves in water with a magenta colour similar to that of Toluylene-red methochloride. It has the formula $C_{18}H_{21}N_4Cl \cdot HCl$ (Found: N = 14.5. $C_{36}H_{42}N_8Cl_4Zn$ requires N = 14.1 per cent.). Attempts to prepare colouring matters from the nitroso-*N*-methyltetrahydroquinoline and *m*-phenylenediamine and tolylenediamine were unsuccessful. The reaction in both cases was very violent and resulted in the formation of insoluble substances, whereas when more dilute acid was used, no colouring matter seemed to be formed.

For purposes of comparison, the following three substances were prepared. They are mentioned by Friedländer (*op. cit.*, Vol. III, p. 397) as possessing a redder shade than the preceding compounds.

*3-Amino-7-methylamino-2-methylphenazine Methochloride
(Formula VII).*

The substance was prepared from nitrosomonomethylaniline hydrochloride and *o*-aminodimethyl-*p*-toluidine dissolved in

alcohol according to the quantities given in D.R.-P. 80758 (Friedländer, *op. cit.*, Vol. IV, p. 376). The mixture was boiled for six hours. The scarlet colour developed in a few minutes and rapidly intensified until a precipitate began to form, when the liquid was somewhat concentrated and cooled. The precipitate was filtered and washed with a little alcohol. The phenazine compound, $C_{15}H_{17}N_4Cl.HCl$, consists of a green, crystalline powder which dissolves in water with a redder shade than the preceding compounds, and at the same time a more magenta shade than the scarlet dyes about to be described.

3-Amino-7-methylamino-2:8-dimethylphenazine Methochloride
(Formula VIII).

The methyl-*o*-toluidine employed in the reaction was obtained by the usual method, namely, by heating together at 200–220° for eight hours *o*-toluidine, methyl alcohol, and hydrochloric acid. The crude base was purified by conversion into the nitrosoamine. Twenty grams were dissolved in 24 c.c. of concentrated hydrochloric acid and 60 c.c. of water, cooled to 0–5°, and 5 grams of sodium nitrite in 15 c.c. of water added slowly with stirring. A pale orange oil separated, and was extracted with ether. It yielded 10 grams of the nitrosoamine. A portion of this was reduced with stannous chloride and gave 4 grams of the pure base, b. p. 206–208°.

Another portion of the nitrosoamine in ether solution was heated (O. Fischer and Hepp, *Ber.*, 1886, 19, 2991) with alcoholic hydrogen chloride on the water-bath and boiled gently under reflux. A white, crystalline deposit slowly formed and after about an hour the precipitation was complete. The crystalline precipitate was filtered and dried. The mother-liquor yielded a further quantity on dilution with ether.

The colouring matter was prepared in the manner described above by boiling together on the water-bath *m*-aminodimethyl-*p*-toluidine in alcohol with nitrosomonomethyl-*o*-toluidine hydrochloride and hydrochloric acid. The yellowish-red colour which first developed intensified rapidly to a much redder shade with no trace of blue, but not so yellow as Azine Scarlet G. The colouring matter partly precipitated in the boiling liquid and was separated by concentration, cooling, filtering, and washing with ether. The compound forms a powder which dissolves in water with a red colour, and has probably the formula $C_{16}H_{19}N_4Cl.HCl$.

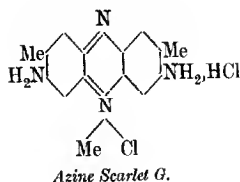
3-Amino-7-benzylamino-2 : 8-dimethylphenazine Methochloride
(Formula IX).

The benzyl-*o*-toluidine was prepared in accordance with Fleischer's method (*Annalen*, 1866, **138**, 228) by heating together at 160° for two hours benzyl chloride (1 mol.) and *o*-toluidine (2 mols.). It boiled at 220°/16 mm. The distillate at once solidified to a colourless mass, m. p. 56—57°. The nitrosoamine described by Kohler (*Annalen*, 1887, **241**, 360) was prepared by the action of sodium nitrite on the base dissolved in dilute sulphuric acid, and melted at 53°. It was dissolved in 20 c.c. of alcoholic hydrogen chloride, and warmed on the water-bath for an hour. The brown nitroso-compound which separated on dilution with ether was used in the crude state for the preparation of the colouring matter. The *p*-dimethylamino-*o*-toluidine dissolved in alcohol with the nitroso-benzyl-*o*-toluidine hydrochloride and hydrochloric acid were heated together on the water-bath as described in the previous preparation. The colour developed, passing from yellowish-red to red with a faintly blue tint, but there was no indication of the brilliant red of Azine Scarlet G. On concentration and cooling, the colouring matter separated, and was filtered and washed with ether. The shade in aqueous solution was slightly bluer than that of the previous compound. It has probably the formula $C_{22}H_{23}N_4Cl.HCl$.

The following series consists of a group of scarlet dyestuffs, including "Azine Scarlet G," some of which are described under D.R.-P. 86608 of the Farbwerke Mühlheim (Friedländer, *op. cit.*, Vol. IV, p. 380). All these compounds contain unsubstituted amino-groups.

3 : 7-Diamino-2 : 8-dimethylphenazine Methochloride
(Azine Scarlet G).

The quantities given in D.R.-P. 86608 (*loc. cit.*) were heated together with stirring at 110°. As the reaction proceeded, much frothing occurred, which subsided when the process was complete (about three hours). The semi-solid, crystalline product was dissolved in nearly boiling water, filtered if necessary, and hydrochloric acid added. On cooling, green, iridescent needles separated. A quantity of the colouring matter remained in the mother-liquor. The substance dissolves in water with a bright scarlet colour (Found: N = 17.5, 17.6. $C_{15}H_{18}N_4Cl_2$ requires N = 17.1 per cent.). The formula is therefore



3 : 7-Diamino-8-methylphenazine Methochloride (Formula III).

The preparation was carried out under similar conditions to the above, a proportionate amount of aminoazobenzene hydrochloride being used in place of the toluene compound. The final product did not crystallise so readily, and required the addition of sodium chloride to assist precipitation. The colouring matter was recrystallised from dilute hydrochloric acid and formed green, iridescent crystals, which dissolved in water with a scarlet colour similar to that described previously (Found: N = 18.5. $C_{14}H_{15}N_4Cl.HCl$ requires N = 18.0 per cent.).

5 : 9-Diamino-10-methylnaphthaphenazine Methochloride
(Formula VI).

The preparation was carried out as above, a proportionate amount of benzeneazo- α -naphthylamine hydrochloride and one and a half times the amount of glycerol being used and heating at 120° being maintained for three and a half hours. Some insoluble matter was formed, which was filtered from the hot aqueous solution. A little salt and hydrochloric acid were used to precipitate the dye. It was recrystallised from dilute hydrochloric acid, the pure product forming green, iridescent crystals. The formula is $C_{18}H_{17}N_4Cl.HCl$. In order to compare the colour of the above with aminophenazines in which one or two amino-groups were substituted for hydrogen in only one nucleus, 2-aminophenazine and 2 : 3-diaminophenazine were prepared.

2-Aminophenazine was prepared by the method of Wohl and Lange (*Ber.*, 1910, **43**, 2186) by heating *o*-nitroaniline and aniline hydrochloride in presence of fused zinc chloride, and also by a method of Kehrman and Harras (*Ber.*, 1913, **46**, 431). The products in the two cases appear to be identical. It crystallises in brilliant red needles, m. p. 283° . It was converted into the acetyl derivative, from which the methochloride was obtained by the action of methyl sulphate in nitrobenzene solution (p. 2059). It

forms a red, crystalline compound. Both the hydrochloride of aminophenazine and the methochloride dissolve in water with a bright magenta colour. The absence of a second amino-group in the second ring seems to produce a similar effect to methylation of the amino-group.

2:3-Diaminophenazine was obtained by the method of Ullmann and Mauther (*Ber.*, 1902, 35, 4302). It was converted into the acetyl derivative and subsequently into the methochloride. The methochloride crystallises in black needles. Both substances dissolve with an orange or orange-red colour in different solvents. Here the presence of a second amino-group in the same nucleus produces a fundamental change in the colour of the substance.

Synopsis of the Principal Dyes of the "Azine Scarlet" Group.

Formula.	Colour in aqueous solution.	Reference.
II.	Magenta	Toluylene Red. D.R.-P. 69188. Fried., Vol. III, p. 397. S. and J., No. 582, p. 228.
I.	Magenta (bluer shade)	Witt, <i>Ber.</i> , 1879, 12, 931. D.R.-P. 15272 (1880).
XV.	Magenta (similar to I)	D.R.-P. 69188.
XVI.	Magenta (similar to II)	"
XVII.	Magenta (similar to I)	"
XII (+ HCl).	Magenta (similar to I)	"
VIII (+ HCl).	Redder than the above	D.R.-P. 80758 (Fried., Vol. IV, p. 376).
IX (+ HCl).	Similar to VIII, but slightly bluer	"
V (+ HCl).	Scarlet	D.R.-P. 86608. Azine Scarlet G. Fried., Vol. IV, p. 380.
II (+ HCl).	Scarlet (similar to IX)	"
V (+ HCl).	Scarlet (similar to IV)	<i>Ber.</i> , 1890, 23, 845.
I (+ HCl).	Scarlet (similar to IV, but less yellow)	D.R.-P. 86608.

Summary.

1. The formation of the quaternary methochloride has only a slight effect on the tint of the parent hydrochloride (I and II).
2. The transition from a simple amino-group through a mono-alkylated to a dialkylated amino-group is accompanied by a gradation in tint from pure scarlet, through scarlet magenta, to pure magenta. The heavier the radicle the bluer the shade (VIII and IX).
3. The transference of both amino-groups to the same nucleus produces a fundamental change in colour.

4. The replacement of a benzene by a naphthalene or tetrahydroquinoline nucleus produces little change in tint.

5. The absence of radicles in the nucleus enhances the blueness of the shade.

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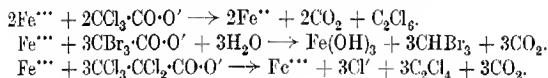
CCXXXVIII.—*The Action of Light of Short Wave-lengths on some Organic Acids and their Salts.*

By FRANS MAURITS JAEGER.

RECENTLY, while studying the velocity of the photochemical decomposition of solutions of the complex oxalate of potassium and tervalent cobalt—a salt which is highly photosensitive—the author observed that this velocity is strongly influenced by the presence of certain cations in the solution. Further examination showed that the progressive addition of neutral salts first increased the velocity in all cases to a maximum, still larger quantities of salt considerably diminished the velocity, and in some cases the photochemical reaction could even be stopped completely by adding enough of the neutral salt. The greater the electrical charge of the cation of the salt added, the smaller was the concentration of the salt required to bring about a maximum velocity of the photochemical reaction. Thus, for instance, the ferric ion brought about a maximal rate at a very small molecular concentration. It was thus that the effect of certain ions on the reactions proceeding under the influence of light radiation was observed, and the observation stimulated the author to take up again older experiments of a like nature. Several years previously he found (*Proc. Roy. Acad. Sci. Amsterdam*, 1911, **14**, 342) that an aqueous solution of trichloroacetic acid, in which freshly-precipitated colloidal ferric hydroxide had been dissolved in an amount insufficient to form a neutral salt, was rapidly decomposed by daylight or by the radiation of the mercury arc. Carbon dioxide was produced and a white, crystalline solid, pure hexachloroethane, C_2Cl_6 , separated. A more detailed study showed that, in particular, the blue, the violet, and the ultra-violet rays act most intensely, in accordance with their maximal specific absorption. The mechanism of the process seemed, however, to be more complicated than was originally supposed; the reaction in dilute solutions was found to differ from

that in concentrated ones. Moreover, the presence of free oxygen has an important effect, in leading to the production of free chlorine and of hydrochloric acid. Although the solutions show all the specific reactions of the free ferric ion, there is no doubt that they contain the iron as a constituent of a complex hexa-trichloro-acetatoferrie ion, which is, however, readily dissociated. If there is no excess of free acid in the solution, the above-mentioned photochemical action does not take place, but another is observed, analogous to the decomposition which occurs when the solution is heated, and resulting in the formation of carbon dioxide and chloroform. If a concentrated solution of trichloroacetic acid is electrolysed between platinum electrodes, the trichloromethyl ester of the acid is formed, as well as carbonyl chloride and hydrochloric acid; the trichloromethyl trichloroacetate in its turn can be split by catalysts into carbon dioxide and hexachloroethane.

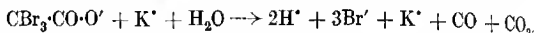
It was further possible to prove that aqueous solutions of ferric tribromoacetate and pentachloropropionate are decomposed photochemically, with formation of carbon dioxide and bromoform, and of tetrachloroethylene respectively. The photochemical processes normally occurring can be expressed by the equations :



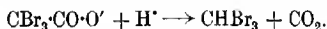
More recently, while studying the influence of light radiation on aqueous solutions of potassium tribromoacetate, it was found that the originally neutral reaction became gradually more and more acid. Added silver nitrate produced a heavy precipitate of silver bromide in increasing quantity as the exposure was prolonged. This observation, in conjunction with what has been said above, suggested a more detailed study of solutions of the potassium salts of this and other similar derivatives of acetic acid when exposed to the radiation of the mercury arc. The photochemical decompositions thus effected were found to differ widely from those observed with the free acids and with their ferric salts under corresponding conditions.

As the behaviour is most evident in the case of tribromoacetic acid, it is advisable to begin with this, as being the least complicated process. When an aqueous solution of potassium tribromoacetate in a quartz vessel is exposed to the rays of a mercury lamp, the course of the reaction depends greatly on the concentration. In dilute solutions, two molecules of hydrobromic acid are formed from each molecule of the salt, while the presence of three equivalents of ionic bromine could be ascertained by gravi-

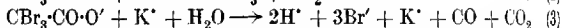
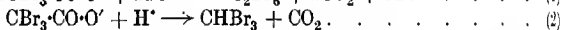
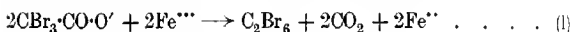
metric analysis. Moreover, the colourless gas which was produced at the same time was subjected to a careful gasometric examination and proved to be an equimolecular mixture of carbon dioxide and carbon monoxide. The latter gas was identified by palladous chloride and estimated quantitatively by absorption in an ammoniacal cuprous chloride solution. The reaction can therefore be completely expressed by the equation :



When, however, more concentrated solutions were treated in the same way, the formation of bromoform as a by-product could be demonstrated, whilst rather less bromine was found on addition of silver nitrate and a smaller quantity of free acid was produced. Evidently a secondary reaction goes on here, which in the case of the pure acid alone would be represented by the equation :



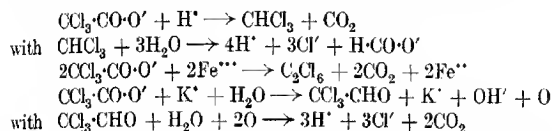
On the other hand, if the ferric salt, in the presence of an excess of free acid, was exposed to the mercury light, the reaction went on in a manner quite analogous to that of ferric trichloroacetate, and resulted in the formation of hexabromoethane and carbon dioxide. The complete set of reactions observed may be expressed by the equations :



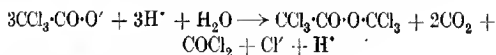
Reaction (2) is an occasional, secondary one. The particular way in which the tribromoacetic ion is decomposed photochemically is therefore evidently very dependent on the presence of special ions in the solution. With ferric ions present, the reaction velocity in this and in other cases is generally much greater than when hydrogen or potassium ions are present. It is not hazardous to suppose that this acceleration is in some way connected with the multiple electrical charge of the ferric ion and the relative facility with which one of the three charges is eventually removed from it.

The reaction produced under the same conditions in a solution of potassium trichloroacetate was found to be of a much more complicated character, the result being evidently a superposition of several different processes, all depending on the prevalence of certain conditions. If the solution of the potassium salt is very concentrated, only an exceedingly small amount of carbon dioxide is generated, and the gas evolved consists almost entirely of carbon monoxide, whilst, at first, for each molecule of carbon monoxide two ions of chlorine seem to be produced. With more prolonged

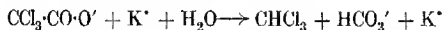
exposures, however, the ratio of chlorinic ions to carbon monoxide gradually falls off, and chloral could be detected in the liquid; the falling off of the ratio is doubtless connected with the probable presence of some free oxygen in the gaseous mixture liberated. In the presence of water and the absence of oxygen, chloral is totally destroyed by light radiation according to the equation $\text{CCl}_3\cdot\text{CHO} + \text{H}_2\text{O} \longrightarrow 3\text{HCl} + 2\text{CO}$, whilst, with oxygen present, the carbon monoxide is partly oxidised to carbon dioxide, and the hydrochloric acid even to chlorine. Although no final equations can be given here for the individual reactions taking place, but only preliminary ones, a general review of all the experimental data obtained may be of use for the purpose of comparison :



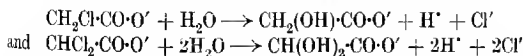
(Schoorl and Van den Berg, *Chem. Zentr.*, 1906, i, 441, 650) and $\text{CCl}_3\cdot\text{CHO} + \text{H}_2\text{O} \longrightarrow 3\text{H}' + 3\text{Cl}' + 2\text{CO}$, at the same time. Depending on the presence of certain other ions in the exposed liquid, the decomposition by the action of light can thus proceed in at least three principal ways, not counting the subsidiary reactions. These reactions differ from those induced by electrolysis or by heat. The electrolytic decomposition is :



and, with catalysts, eventually $\text{CCl}_3\cdot\text{CO}\cdot\text{O}\cdot\text{CCl}_3 \longrightarrow \text{CO}_2 + \text{C}_2\text{Cl}_6$. The thermal decomposition is :

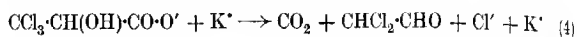


The photochemical decomposition of mono- and dichloroacetic acids has already been studied by Beurath (*Annalen*, 1911, **382**, 222) and by Euler and Cassel (*Zeitsch. physikal. Chem.*, 1913, **84**, 371). The reaction proceeds according to the schemes :

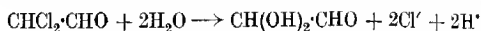


These reactions are of some interest in connexion with the behaviour of the potassium salt of *trichlorolactic acid*, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{OH}$, when exposed to mercury rays. In that case, evidently only an insignificant quantity of free acid is generated, but for each molecule of the potassium salt 1 molecule of carbon dioxide is set free and one equivalent of chlorine is found to be present as ion. If the

solution after exposure is feebly acidified with acetic acid and heated with semicarbazide hydrochloride, a yellow, crystalline product is obtained, which proves to be the disemicarbazone of glyoxal. According to Harries and Temme (*Ber.*, 1909, **40**, 171) and to Kling (*Bull. Soc. chim.*, 1909, [iv], **5**, 412), this fact indicates the original presence of dichloroacetaldehyde, which by a secondary reaction is transformed to glyoxal hydrate when heated with a feebly acid solution of semicarbazide. The photochemical reaction can therefore be represented by the equation:

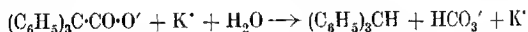


whilst the secondary, purely chemical change occurs as follows:

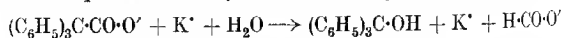


It may be remarked that the photochemical transformation is in this case accompanied, or immediately followed, by an intramolecular rearrangement of the atoms, and that the photochemical process does not differ here from the thermal decomposition, for aqueous solutions of the potassium salt are likewise decomposed on heating according to equation (4) above.

In continuation of the above experiments, the photochemical decomposition of triphenylacetic acid has been studied in some detail. Both the acid and its potassium salt are only sparingly soluble, and therefore solutions in alcohol-water mixtures of various concentrations were employed. In dilute solutions, the photochemical reaction rapidly results in the liberation of carbon dioxide, which dissolves in the liquid, and in the production of a white, crystalline solid, which after recrystallisation proves to be pure triphenylmethane (m. p. 93°), whilst the solution gradually becomes alkaline:



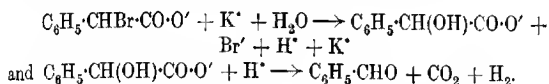
In more concentrated solutions, an additional change takes place and a crystalline mixture is deposited which for the most part consists of triphenylcarbinol (m. p. 163°), dissolving in concentrated sulphuric acid with a yellow colour. This second photochemical process evidently occurs according to the scheme:



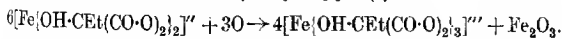
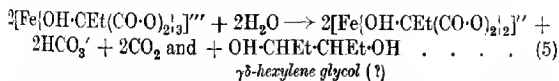
whilst the formate produced is partly decomposed.

In analogous circumstances, phenylbromoacetic acid, as potassium salt, is readily decomposed without liberation of carbon dioxide. In the liquid, a considerable amount of ionic bromine could be demonstrated. On closer examination, it could be shown that for each molecule of the salt one equivalent of bromine is precipitated

as silver bromide, whilst the characteristic odour of benzaldehyde is noticed. Evidently the original photochemical process consists in the formation of mandelic acid, which in its turn is split into benzaldehyde and formic acid. Since the solutions were stirred by a current of air, so that free oxygen was present, the secondary reactions are partly also those studied by Berthelot and Gaudechon (*Compt. rend.*, 1910, **150**, 1690; **151**, 1349; 1911, **152**, 262; **153**, 383; 1913, **157**, 333) in the case of mandelic acid, and by Benrath (*Annalen*, 1911, **382**, 222; *J. pr. Chem.*, 1917, [ii], **204**, 190) and Ciamician and Silber (*Ber.*, 1913, **46**, 1558) in the case of formic acid, when exposed to such radiation under the same conditions. In its principal features, the sequence of reactions occurring here may be represented thus:



Finally, some preliminary experiments were made with the yellowish-green ferric complex salt of ethyltartronic acid, or rather with the potassium salt of the complex ferrietri(ethyltartronic) ion, the solution of which is very sensitive to the action of light. The green solution became colourless, carbon dioxide was produced, and the liquid reduced silver nitrate solution immediately with formation of finely-divided, black, metallic silver. On keeping or passing oxygen into it, the colourless solution gradually resumes a green colour and then the original salt can be precipitated by alcohol. Evidently the photochemical reaction in this case is completely analogous to the well-known photochemical reduction of potassium ferric oxalate to potassium ferrous oxalate. The latter salt is also a very effective reducing agent for silver salts, and is easily reoxidised by free oxygen to the original ferric salt. If this be so—and by further investigation the author hopes to confirm this—the photochemical process (5) and the subsequent oxidation may probably be represented by the equations:



One product of the first reaction has an agreeable aromatic odour, reminiscent of celery leaves, but its identity can be established only by further experiment.

We may state, in conclusion, by way of summary, that the various photochemical reactions of the substances dealt with are

in each case truly specific, and are directly comparable neither to the effects of electrolysis nor, in most cases, to those of heat. Both electrolytic and thermal effects have occasionally been considered analogous to photochemical change. The above and other experiments enable us to emphasise once more that in the case of photochemical change no such general comparisons are valid; each photochemical reaction is specific and very dependent on the conditions obtaining at the moment, so that it is scarcely ever possible to predict its course. Among the conditions governing the reaction, the presence of certain ions in the solution must be considered a factor of great importance.

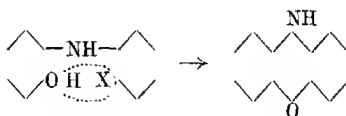
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[Received, October 8th, 1921.]

CCXXXIX.—A New Synthesis of Oxazines.

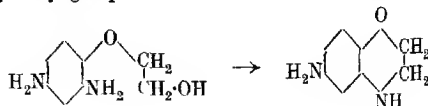
By ARTHUR FAIRBOURNE and HAROLD TOMS.

SYNTHESES of oxazines are usually brought about by the preliminary formation of a nitrogen linking, followed by the completion of an oxazine ring, according to the following scheme:



This has the disadvantage, however, of affording no simple method of preparation of amino-derivatives, the reduction of nitro-oxazines being by no means easy; and it otherwise very greatly limits the type of substance obtainable.

Research now in progress (compare the previous paper, this vol., p. 1036) has resulted in a different formation of oxazines, which is the converse of the usual process, that is, it consists in the closing of a simple ether chain by the elimination of water from an amino- and a hydroxyl-group:



The oxazines being of very considerable interest, both technically (compare Justin-Mueller, *Rev. Gen. Col.*, 1920, **24**, 130; also, in connexion with amino-derivatives, Kehrman, *Ber.*, 1905, **36**, 481, 483) and, more especially, scientifically (compare Knorr, *Ber.*, 1899, **22**, 1209; Kehrman, *loc. cit.*, p. 479), this alternative and rather unexpected possibility of their synthesis appears sufficiently useful to be put on record, the only previous example of a preparation in any way similar which has come to the notice of the authors being a condensation of amino- and carboxyl-groups (Bischoff, *Ber.*, 1900, **33**, 1593), the carbonyl of the latter remaining in the ring produced, and not readily allowing of reduction to the parent oxazine.

EXPERIMENTAL.

2:4-Dinitrophenyl β -Hydroxyethyl Ether, and its Reduction.

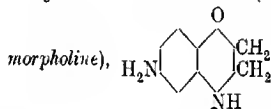
This substance was prepared by a method similar to that employed in the case of the corresponding ether of glycerol (*loc. cit.*), a small quantity of aqueous sodium hydroxide solution proving successful, however, as condensing agent instead of the sodium derivative of ethylene glycol. To a solution of 8.1 grams of 1-chloro-2:4-dinitrobenzene in 18 c.c. of ethylene glycol was added an ethylene-glycollic solution of sodium hydroxide (1 mol.) obtained by dissolving 1.6 grams of the solid alkali in 1 c.c. of water and adding 18 c.c. of the glycol. The mixture was heated on a water-bath for half an hour, during which time crystals of sodium chloride separated. While still hot, the liquid was stirred into 50 c.c. of water, from which, on cooling, were deposited 8.5 grams of acicular crystals. These were recrystallised from 20 per cent. acetic acid and from water, and were then colourless and melted at 109° (Found: C = 42.15; H = 3.75; N = 12.47. Calc., C = 42.11; H = 3.51; N = 12.29 per cent.).

The mother-liquor from the acetic acid crystallisation contained a small quantity of another substance, m. p. 192–195°, which was not sufficient to admit of complete analysis, but an estimation of the nitrogen indicated that the compound was ethylene glycol bisdinitrophenyl ether, $C_6H_4(O-C_6H_3(NO_2)_2)_2$. In other experiments, the ethylene-glycollic sodium hydroxide was prepared by pouring the strong aqueous alkali into the glycol, instead of pouring the glycol into the aqueous alkali, and in the subsequent condensations with chlorodinitrobenzene no trace of the bisdinitrophenyl ether could then be found. It would consequently appear that the presence of excess of the glycol during the whole period of the preparation of the glycollic alkali prevented the formation of the

disodium derivative of glycol, and consequently of the bisdinitrophenyl ether also.

Reduction of 2:4-Dinitrophenyl β -Hydroxyethyl Ether.—One part by weight of the monophenyl ether was gradually added to twenty-two parts of water containing two parts of iron and a small quantity of hydrochloric acid, the addition being extended over a quarter of an hour, and being carried out at 74–76°. The whole was maintained at this temperature for a further equal period of time, the product was then filtered and the residue extracted with boiling water. As the resulting diamine was found to be insoluble in ether, and exceedingly difficult to purify in any form, the water was evaporated and the dried material was submitted to dehydration in the crude state, as described below. No specimen of this free diamine has been isolated, but, by boiling the crude product with excess of acetyl chloride and then decanting and diluting the solution obtained, long, colourless needles of the triacetyl derivative were isolated, m. p. 128–130° (Found: $\text{CH}_3\cdot\text{CO} = 43.1$. Calc., $\text{CH}_3\cdot\text{CO} = 43.8$ per cent.).

6-Amino-2:3-dihydro-1:4-benzisooxazine (6-Aminobenzo-



The crude diamine mentioned above was dissolved in 10 parts by weight of concentrated sulphuric acid, and heated slowly to 150°, at which temperature it was maintained for several minutes. The product was cooled, poured into water, and extracted with ether after neutralisation with sodium hydroxide. The ethereal extract was dried over solid sodium hydroxide, and the ether was removed by evaporation, when a mass of colourless, acicular crystals was obtained, which, after recrystallisation from water, melted at 80° (Found: N = 18.9. Calc., N = 18.6 per cent.).

The authors wish to express their indebtedness to the Chemical Society for a grant to one of them (H. T.) which has partly defrayed expenses incurred in this work.

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CCXL.—*The Influence of Neutral Salts on the Hydrolysis of Ethyl Formate.*

By ALEXANDER BERNARD MANNING.

NEUTRAL salt action, as ordinarily measured, is probably due to two or more causes acting together, and the difficulty in explaining the total effect in any particular example lies in disentangling these causes and assigning to each its specific effect.

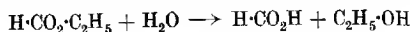
If to a solution of an electrolyte HA we add a neutral salt BC, there will be in general a change in the concentration of the ion H^+ owing to the formation of the new molecular species HC and BA and the consequent readjustment of the concentrations of the ions present. The change in concentration of H^+ due to this cause may be called the *true* neutral salt action.

Of other effects often included under neutral salt action the most prominent is due probably to *hydration* and the consequent changes in concentration of the solvent. To quote one instance—it is known that the presence of potassium chloride increases the rate at which sucrose is hydrolysed by an acid, but a comparable increase in velocity of hydrolysis can be produced also by the presence of a neutral non-electrolyte, for example, mannitol (Rosanoff and Potter, *J. Amer. Chem. Soc.*, 1913, **35**, 248), or indeed sucrose itself, for the rate of hydrolysis increases considerably with initial concentration of sugar. In all investigations on neutral salt action an attempt should be made to estimate the hydration factor by a careful comparison of the effect of addition of the neutral salt with that of the addition of some otherwise inactive non-electrolyte, the hydration effect of which has been otherwise determined. This was done in the work described below, and by a fortunate chance it was found that the method chosen was practically independent of hydration effects, glucose and sucrose even in considerable concentrations producing inappreciable changes in the particular reaction constant measured. On the assumption that there are no other disturbing influences, the following experimental work should give a measure of the *true* neutral salt action as defined above. The results will be discussed from this point of view.

EXPERIMENTAL.

Dilute aqueous solutions of ethyl formate (1–2 per cent.) hydrolyse at a conveniently measurable rate at 25°, in the absence of acid other than that produced by the hydrolysis. The course of

this reaction in water alone and in solutions of various neutral salts and non-electrolytes has been studied. The reaction



is autocatalytic and for dilute solutions of the ester can be taken as complete.

To obtain an expression for the course of the change it will be assumed, as a working hypothesis, that the rate of hydrolysis is jointly proportional to the concentration of the ester and of the hydron.

Let a = the initial concentration of ester.

x = the concentration of formic acid produced after time t .

c = the concentration of undissociated formic acid at time t .

c_1 = concentration of hydron at time t .

$$\text{Then } c + c_1 = x \quad \dots \dots \dots (1)$$

$$\text{And } \frac{c_1^2}{c} = k_1, \text{ the ionisation constant of formic acid at } 25^\circ \dots \dots \dots (2)$$

The above assumption gives

$$\frac{dx}{dt} = K(a - x)c_1 \quad \dots \dots \dots (3)$$

We may call K the *reaction constant*.

Eliminating c and c_1 from (1), (2), and (3), we have

$$\frac{dx}{dt} = \frac{1}{2}Kk_1(a - x)\left\{\sqrt{1 + \frac{4x}{k_1}} - 1\right\}.$$

This gives on integration

$$\begin{aligned} & \frac{1}{2}[2 \log \{\sqrt{1 + k'x} - 1\} + (\sqrt{1 + k'a} - 1) \log \{\sqrt{1 + k'a} + \\ & \quad \sqrt{1 + k'x} - (\sqrt{1 + k'a} + 1) \log \{\sqrt{1 + k'a} - \sqrt{1 + k'x}\} \\ & = 2aK(t_1 - t_0), \text{ where } k' = \frac{4}{k_1} \dots \dots \dots (4) \end{aligned}$$

Initially the hydroxyl ions of the water also catalyse the reaction, but with increasing concentration of the hydrogen ions that of the hydroxyl ions soon becomes inappreciable. This initial effect is readily seen to be negligible in the present case.

The reaction was followed by titration with $N/20$ -ammonia, with methyl-red as indicator. The use of a stronger alkali, such as baryta, was found to be inadmissible, since it appeared to catalyse the reaction appreciably during the titration, particularly during the early part of the reaction. This suspicion was confirmed by following the reaction (a) using baryta, (b) using ammonia, (c) by

the electrical conductivity method. (a) invariably gave higher values for the amount of hydrolysis than (b) or (c) except towards the end of the reaction. The values from (b) and (c) agreed within the limits of the experimental error.

The ethyl formate used was carefully purified and was freshly distilled immediately before each series of experiments. A litre of water, or of the solution to be used, was placed in a stoppered Jena glass bottle in a thermostat at $25^{\circ} \pm 0.05^{\circ}$. When this had attained the temperature of the bath, the requisite amount of ester was pipetted into it, the bottle shaken thoroughly, and the time taken. At convenient intervals 25 c.c. of the solution were removed and titrated with the standard ammonia. The initial concentration of ester was determined exactly by adding excess of baryta to 25 c.c. of the solution, keeping for two days, and titrating the excess of baryta with hydrochloric acid, care being taken to exclude carbon dioxide.

All the salts used were recrystallised at least once. Conductivity water was used throughout for the solutions.

When using a solution of a salt or non-electrolyte, a correction was made for the alteration in concentration of the solution due to the small change in volume on addition of the ester.

The Rate of Reaction with Water alone.

Initial concentration of the ester 0.0578 <i>M</i> .			Initial concentration of the ester 0.1163 <i>M</i> .			Initial concentration of the ester 0.1745 <i>M</i> .		
Time in hours.	Amount changed per cent.	<i>K</i> .	Time in hours.	Amount changed per cent.	<i>K</i> .	Time in hours.	Amount changed per cent.	<i>K</i> .
2.97	0.64	—	2.77	1.04	—	6.72	5.90	—
22.97	15.3	4.81	5.42	2.70	4.88	24.02	43.95	4.73
25.3	18.0	4.78	22.5	29.32	4.81	28.42	54.6	4.76
29.85	24.15	4.81	24.93	34.4	4.82	30.62	59.25	4.79
46.87	48.1	4.82	27.37	39.3	4.82	48.35	85.3	4.79
53.45	56.5	4.81	30.08	44.9	4.83	55.17	90.3	4.79
70.62	74.5	4.84	46.50	72.4	4.85	72.25	96.6	4.72
72.93	76.4	4.84	49.07	75.6	4.85	78.73	97.9	4.79
			54.03	80.9	4.86			
			70.58	91.7	4.85			
Mean <i>K</i> = 4.82			Mean <i>K</i> = 4.84			Mean <i>K</i> = 4.77		

The constancy of the calculated values of *K* fully justifies the assumptions made in deducing equation (4).

In the experiments in presence of neutral salts or non-electrolytes, the concentration of ester used was in the region of 0.116*M*. The average of several determinations of *K* for water alone and for concentrations of ester between 0.115*M* and 0.117*M* was 4.83. This will be taken as the basis for comparison with the values obtained in the presence of other substances.

The Rate of Reaction in Solutions of Non-electrolytes.

Glucose was the non-electrolyte principally studied; the following are typical results.

M/4-Glucose. Conc. of the ester = 0.1163M.			2M-Glucose. Conc. of the ester = 0.1160M.		
Time in hours.	Amount changed per cent.	K.	Time in hours.	Amount changed per cent.	K.
4.23	1.50	—	3.47	0.83	—
6.87	3.43	4.88	22.93	28.02	4.85
8.83	5.41	4.87	25.38	33.5	4.90
23.38	30.46	4.87	29.73	43.2	4.96
25.73	35.55	4.90	46.53	73.3	5.06
28.30	40.76	4.88	52.2	79.6	5.04
33.12	50.63	4.91	71.4	91.7	4.90
47.83	74.13	4.92			
52.50	79.32	4.92			
56.57	83.3	4.93			
73.37	93.0	4.93			
97.67	97.9	4.82			

Mean $K = 4.89$ Mean $K = 4.95$

In M/10-glucose, the mean $K = 4.84$; and in M-glucose, the mean $K = 4.92$.

There appears to be a very slight, gradual increase in K with increasing concentration of glucose, but, as will be seen later, it is very small compared with the increase in the presence of neutral salts.

Similar results are obtained with solutions of sucrose. Thus in

M/2-sucrose, the mean $K = 4.92$.

M-sucrose, the mean $K = 5.10$.

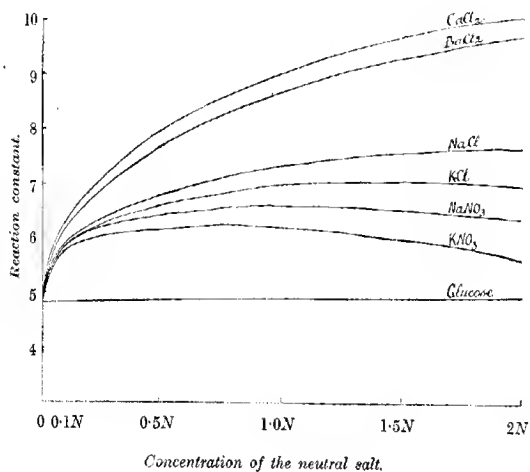
*The Rate of Reaction in Solutions of Neutral Salts.**Typical results in solutions of potassium chloride.*

Conc. of KCl = 0.0993N.			Conc. of KCl = 0.495N.			Conc. of KCl = 1.99N.		
Initial conc. of the ester = 0.1165N.			Initial conc. of the ester = 0.1165N.			Initial conc. of the ester = 0.1158N.		
Time in hours.	Amount changed per cent.	K.	Time in hours.	Amount changed per cent.	K.	Time in hours.	Amount changed per cent.	K.
5.78	3.47	—	4.08	2.72	—	1.73	1.22	—
22.56	37.9	5.78	6.08	5.25	6.52	6.53	7.31	6.82
25.65	45.0	5.77	8.08	8.54	6.45	23.03	52.1	6.96
29.52	54.0	5.79	22.5	45.5	6.53	25.72	58.8	6.95
46.73	82.3	5.85	27.27	57.7	6.54	30.5	69.6	6.98
51.43	86.7	5.85	29.33	62.4	6.54	47.23	90.7	6.97
53.63	88.8	5.92	46.93	88.0	6.55	49.68	92.1	6.93
71.5	96.6	5.93	49.38	89.7	6.52	71.10	98.4	6.87
78.2	97.7	5.94						

Mean $K = 5.85$ Mean $K = 6.52$ Mean $K = 6.93$

The results similarly obtained with solutions of sodium chloride, potassium nitrate, sodium nitrate, calcium chloride, and barium chloride are tabulated below and represented graphically in Fig. 1.

FIG. 1.

*Values of K for Various Salts.*

Conc. of salt.	KCl.	NaCl.	KNO ₃ .	NaNO ₃ .	CaCl ₂ .	BaCl ₂ .
N/10	5.85	5.89	5.76	5.87	6.23	6.15
N/4	6.18	—	6.01	6.17	—	6.81
N/2	6.53	6.75	6.14	—	7.90	7.61
N	6.94	7.28	6.15	6.53	8.95	8.63
2N	6.93	7.62	5.54	6.38	10.0	9.65

In all the solutions of these salts the constancy of the values of *K*, calculated throughout the course of the reaction, was very satisfactory. Moreover, the result of addition of the salt was always to accelerate the reaction. Solutions of the sulphates behave differently. Potassium and sodium sulphates retard the reaction, and show a gradual increase in *K* as the reaction proceeds.

Below are results for potassium sulphate:

Conc. of $K_2SO_4 = 0.0991N$.			Conc. of $K_2SO_4 = 0.992N$.		
Initial conc. of the ester = $0.1163N$.			Initial conc. of the ester = $0.1163N$.		
Time in hours.	Amount changed per cent.	K .	Time in hours.	Amount changed per cent.	K .
3.43	1.04	—	2.62	0.94	—
4.95	1.56	3.22	5.13	1.77	3.00
6.03	2.18	3.69	7.98	3.22	3.17
22.92	23.4	4.14	22.0	18.6	3.58
25.35	27.65	4.15	24.47	22.45	3.63
29.67	35.75	4.19	28.83	29.6	3.68
46.47	63.9	4.26	45.63	57.3	3.82
52.15	71.3	4.27	51.6	65.2	3.84
71.37	87.5	4.28	70.53	83.6	3.90
95.7	96.1	4.30	94.37	93.8	3.98
Mean $K = 4.06$			Mean $K = 3.61$		

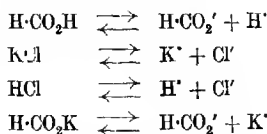
Sodium sulphate gives similar results.

Discussion of Results.

It has been shown that solutions of glucose and sucrose of relatively high concentrations give very nearly the same values for the reaction constant K as does water alone. Unless, therefore, in solutions of these non-electrolytes there are two or more effects exactly annulling each other, which is improbable, it may be concluded that the rate of reaction is independent of changes in the concentration of the water. In other words, hydration of the solute does not affect K .

It may further be remarked that changes of viscosity have here little effect on the rate of reaction.

Admitting no further hypothesis, we must take the change in K on addition of neutral salts as due to an actual change in the concentration of hydrogen ions in the solution, K indeed giving a measure of the change. This change is a result of the readjustment in concentrations on addition of the neutral salt (say, potassium chloride) conditioned by the equilibria:



It remains to be seen whether the theory of such mixtures of electrolytes, as far as it has been developed up to the present, will lead to the same results as those obtained experimentally.

Of the four equations above, three represent the dissociation of strong electrolytes. For dealing with such mixed electrolytes as

these Arrhenius (*Zeitsch. physikal. Chem.*, 1899, **31**, 197; compare also Sherrill, *J. Amer. Chem. Soc.*, 1910, **32**, 741) proposed the following form of "dilution law":

$$\frac{B' \times A'}{BA} = D(\Sigma i)^m,$$

where BA is one of the electrolytes, dissociating into the ions B' and A', Σi is the sum of the ionic concentrations, that is, the total concentration of positive (or negative) ions in the solution, and D and m are constants.

Following the method proposed by Arrhenius, the concentrations of hydrogen ion in various mixtures of potassium chloride, sodium chloride, barium chloride, and potassium sulphate respectively with formic acid have been calculated. There is, however, another point to be considered in comparing the calculated with the experimental results. During the reaction the concentration of formic acid varies, increasing from zero to slightly more than 0.1N. The fact that a constant value is obtained for K throughout the reaction (except for the sulphates) shows that for the same concentration of neutral salt the same proportional increase in hydrogen-ion concentration is produced, independently of the concentration of acid.

As an example, consider a solution containing 0.1N-formic acid in the presence of N-potassium chloride. In 0.1N-formic acid alone the concentration of hydrogen-ion is 0.00452 gram-ion per litre. In the mixed solution the concentrations of the various ions and molecules present are given by the following simultaneous equations:

$$\frac{K' \times Cl'}{KCl} = K_1(K' + H')^m,$$

$$\frac{H' \times Cl'}{HCl} = K_2(K' + H')^m,$$

$$\frac{K' \times H \cdot CO_2'}{H \cdot CO_2 K} = K_3(K' + H')^m,$$

$$\frac{H' \times H \cdot CO_2'}{H \cdot CO_2 H} = K_4(K' + H')^m,$$

$$K' + KCl + H \cdot CO_2 K = 1$$

$$Cl' + KCl + HCl = 1$$

$$H' + HCl + H \cdot CO_2 H = 0.1$$

$$HCO_2' + H \cdot CO_2 H + H \cdot CO_2 K = 0.1.$$

The values of the constants, found from the conductivity data,

assuming the conductivity-viscosity ratio to give the degree of dissociation, are

$$K_1 = 2.44; K_2 = 5.25; K_3 = 1.15; K_4 = 0.000214.$$

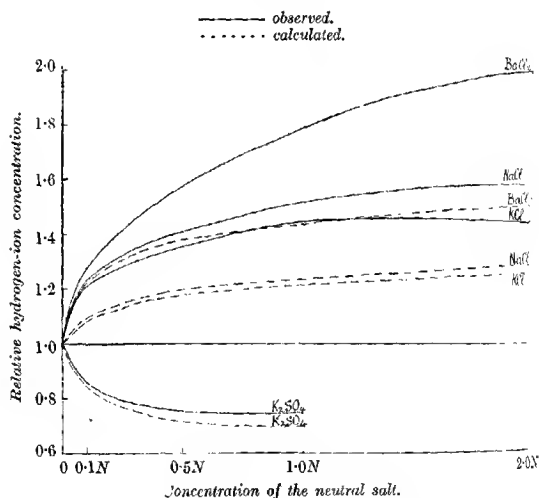
$$m_1 = 0.62; m_2 = 0.62; m_3 = 0.54; m_4 = 0.$$

Solving the equations, we have

H^+	$= 0.00547$	K^+	$= 0.731$
HCO_2^+	$= 0.00366$	Cl^+	$= 0.733$
KCl	$= 0.266$	$H \cdot CO_2H$	$= 0.0936$
HCl	$= 0.000924$	$H \cdot CO_2K$	$= 0.00274$

Thus the addition of the neutral salt has increased the hydrogen-ion concentration from 0.00452 to 0.00547 gram-ion per litre. The

FIG. 2.



increase is 21.0 per cent. The same percentage increase is produced with smaller initial concentrations of formic acid. Thus in 0.05N-formic acid the hydrogen-ion concentration is 0.003165 gram-ion per litre. In the presence of N-potassium chloride this becomes 0.00383 gram-ion per litre. The increase again is 21.0 per cent.

In the diagram (Fig. 2) is shown the calculated percentage increase in concentration of hydrogen ion in the presence of various concentrations of potassium, sodium, and barium chlorides and

potassium sulphate respectively. The observed values also are shown, drawn to the same scale.

Calculation of the hydrogen-ion concentration in mixtures of potassium sulphate and formic acid shows a decrease on addition of the neutral salt. Thus :

H-ion conc. in 0.1N-formic acid .	0.00452	gram-ion	per litre.
H-ion conc. in 0.1N-formic acid in presence of 0.1N-K ₂ SO ₄ .	0.00381	"	"
H-ion conc. in 0.1N-formic acid in presence of N-K ₂ SO ₄ .	0.00325	"	"

Moreover, the decrease is not quite proportional to the original hydrogen-ion concentration. Thus in presence of N-potassium sulphate the hydrogen-ion concentration of 0.1N-formic acid decreases to 72 per cent., that of 0.05N-formic acid to 71 per cent., and that of 0.01N-formic acid to 67 per cent. of the original. Some variation in the value of K , then, is to be expected.

With the sulphates the agreement of calculated and experimental results is good. With the chlorides, however, the observed values are considerably greater than the calculated. It is true that some of the data used in the derivation of the constants in Arrhenius's formula are not very trustworthy. This applies particularly to the conductivity data for the formates in aqueous solution at 25°, which need redetermining. But the results indicate that some modification of Arrhenius's mixture law is necessary. Again, it may be noted that the nitrates show clearly, and potassium chloride gives some indication of, a maximum neutral salt effect with increasing concentration. The method of calculation used above would give no maximum. It would, however, seem useless to test any other mixture law until more trustworthy data are available or the dissociation of the formates in solution.

[NOTE.—The work described above was begun in 1914, but, very shortly after its commencement, had to be postponed until 1919. Later, it had again to be put aside, and as, at the moment, circumstances do not permit its continuation, it is being published in its present, somewhat incomplete, form.]

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

SOUTH KENSINGTON.

[Received, September 16th, 1921.]

CCXLI.—*The Action of Diazo-salts on Aromatic Sulphonamides. Part I.*

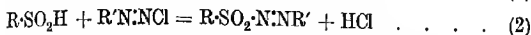
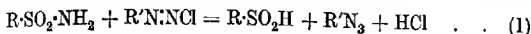
By PAVITRA KUMAR DUTT, HUGH ROBINSON WHITEHEAD, and ARTHUR WORMALL.

HINSBERG (*Ber.*, 1894, 27, 598), by the action of benzenediazonium chloride on benzenesulphonamide in very dilute alkaline solution, obtained a yellow, crystalline product, which in the crude state melted at 102° with decomposition and on analysis gave 15.63 per cent. of nitrogen. From this, the author assigned to it the structure $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{N}\cdot\text{NPh}$, which requires 16.09 per cent. of nitrogen. On warming with dilute acids or alkalis, it decomposed into benzenesulphonamide, phenol, nitrogen, and a resinous product.

In repeating Hinsberg's reaction with molecular quantities of *p*-toluenesulphonamide and benzenediazonium chloride, we obtained a yellow, crystalline product which, however, smelt strongly of phenylazoimide. On recrystallisation from dilute alcohol, it melted at 95° (with decomposition), and its analysis agreed with the formula $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{N}\cdot\text{NPh}$. A similar compound isomeric with the above, *p*-toluenediazobenzenesulphonate, $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, had previously been prepared by Hantzsch and Singer (*Ber.*, 1897, 30, 312) by the action of *p*-toluenediazonium chloride on benzenesulphinic acid, and the lower homologue, $\text{SO}_2\text{Ph}\cdot\text{N}\cdot\text{NPh}$, by Königs (*Ber.*, 1877, 10, 1531) by the action of benzenediazonium chloride on the same substance. On the other hand, when the crude yellow product was crystallised from benzene and light petroleum, it melted sharply at 87–88°, with decomposition, and its analysis agreed with the formula $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{N}\cdot\text{NPh}$.

Assuming that the diazo-sulphonate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{N}\cdot\text{NPh}$, had been formed in a similar way to that of Königs and of Hantzsch and Singer, we concluded that the diazoamino-compound, first formed must have decomposed in presence of alkali into *p*-toluenesulphinic acid and phenylazoimide, and the sulphinic acid thus formed must have combined with the benzenediazonium chloride. This has been verified by carrying out the condensation in presence of a large excess of alkali, when no solid but phenylazoimide was obtained in very good yield. The sulphinic acid present in the alkaline aqueous portion was converted into the insoluble ferric salt (Thomas, *T.*, 1909, 95, 342). The yield was almost quantitative, according to equation (1). In another experiment the sulphinic acid was condensed with a molecular proportion of the diazonium salt, when

the diazosulphinate was obtained in very good yield, the reaction taking place according to equation (2).



Hinsberg's product may therefore be regarded as a mixture of the diazoamino-compound, $\text{R}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{N}\cdot\text{NR}'$, and the diazo-sulphinate, $\text{R}\cdot\text{SO}_2\cdot\text{N}\cdot\text{NR}'$. This reaction has been studied with both benzene- and *p*-toluene-sulphonamides on the one hand, and aniline, *o*-, *m*-, and *p*-toluidines, and *p*-chloroaniline on the other. The products in all cases are similar and the reaction may be represented by equations (1) and (2). The reaction, therefore, can conveniently be utilised for the preparation of aromatic azoimides and sulphinic acids.

EXPERIMENTAL.

Action of Benzenediazonium Chloride on p-Toluenesulphonamide.

Experiment I.—Benzenediazonium chloride (made from aniline, 4.6 grams, hydrochloric acid, 15 c.c., and water, 25 c.c., diazotised with sodium nitrite, 3.5 grams in water, 15 c.c.) was slowly added to a well-cooled solution of 8.5 grams of *p*-toluenesulphonamide and 6 grams of sodium hydroxide in 175 c.c. of water. The mixture was stirred for about ten minutes and filtered, and the yellow, crystalline product washed with water and dried in a vacuum desiccator. The filtrate was slightly alkaline and smelt strongly of phenylazoimide. The crude product melted and decomposed at 83–85° (Found: N = 13.9 per cent.). The yield was 8 grams. A portion, recrystallised from aqueous alcohol, formed yellow needles, m. p. 95° with decomposition (Found: C = 59.78 by the wet method; N = 10.98; S = 12.34. *Benzenediazo-p-toluenesulphinate*, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{N}\cdot\text{NPh}$, requires C = 60.00; N = 10.77; S = 12.31 per cent.). The sulphur was estimated by fusion with potassium carbonate and potassium nitrate, as an attempt by the Carius method resulted in an explosion just after the tube had been sealed.

The diazo-sulphinate, on reduction with zinc dust and acetic acid in alcoholic solution (Königs, *loc. cit.*), gave the colourless dihydro-derivative. This, when recrystallised from alcohol, formed needles, m. p. 154° with decomposition (Found: N = 10.9. $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}\cdot\text{NHPh}$ requires N = 10.7 per cent.).

A small portion of the crude condensation product, m. p. 83–85°, mentioned above, was dissolved in a large volume (1 gram in 50 c.c.)

of benzene at about 30° and filtered. The pale yellow, crystalline precipitate that separated on adding light petroleum to the cooled filtrate was quickly collected and dried in the dark; it melted sharply with decomposition at 87–88° (Found: N = 15.55. The diazoamine, $\text{CH}_2\text{-C}_6\text{H}_4\text{-SO}_2\text{-NH}\cdot\text{N}\cdot\text{NPh}$ requires N = 15.27 per cent.). When warmed with sodium hydroxide solution, contrary to Hinsberg's statement, it liberated phenylazoimide. In alcoholic solution, it gave a deep red coloration with a solution of β -naphthol.

Experiment II.—In this experiment the reaction was carried out in presence of a large excess of alkali. Benzenediazonium chloride (made from 9.3 grams of aniline) was slowly added to a solution of 17 grams of *p*-toluenesulphonamide and 15 grams of sodium hydroxide in 350 c.c. of water. In this case no precipitate was formed, but an orange, opalescent liquid was obtained smelling strongly of phenylazoimide. A drop of the liquid produced a deep red coloration on β -naphthol test-paper. A few c.c. of the liquid were acidified with cold dilute acetic acid and gave a pale yellow precipitate, which, after being filtered, washed, and dried, melted with decomposition at 85–86° (Found: N = 15.28 per cent.). The reaction mixture, which evidently contained the diazoamine in solution, showed no appreciable decomposition even after being stirred for two hours. The mixture having been kept overnight in the ice box, a considerable amount of oil had accumulated at the bottom of the vessel, but the liquid still gave the red coloration with β -naphthol test-paper. Sodium hydroxide (15 grams) was then added and the mixture stirred until no colour reaction was obtained with β -naphthol paper. It was then extracted with ether, the ether distilled off, and the residue distilled in steam. The steam distillate was again extracted with ether, and the extract dried over calcium chloride and distilled in a vacuum from a water-bath. The yield of phenylazoimide was 9 grams, the calculated yield being 11.4 grams according to equation (1). It is a clear yellow liquid, having a characteristic, penetrating, but not unpleasant smell. It explodes when heated in a test-tube over a Bunsen flame, but distils at 81° under 44 mm. pressure. To identify the product further, it was condensed with ethyl acetate, a substance, melting at 115°, being produced identical with that obtained by Dimroth (*Ber.*, 1902, 35, 4057) from phenylazoimide and ethyl acetate.

The aqueous solution left after the phenylazoimide had been removed was divided into two equal portions. One portion was acidified with hydrochloric acid. The brick-red precipitate obtained by the addition of ferric chloride to the acid solution was collected (yield 8.5 grams, the calculated yield being 8.7 grams), treated with a slight excess of aqueous ammonia, and filtered. On the

addition of concentrated hydrochloric acid to the cooled filtrate, colourless, crystalline *p*-toluenesulphinic acid was precipitated. It was recrystallised from water and melted at 86–87° (Thomas gives m. p. 86–87°, *loc. cit.*). It gave the characteristic blue colour reaction of aromatic sulphinic acids with concentrated sulphuric acid and anisole (Smiles and Rossignol, T., 1906, 89, 696) (Found : S = 20.54. Calc., S = 20.51 per cent.).

The other portion of the aqueous solution mentioned above was treated with half the quantity of benzenediazonium chloride, when a yellow, crystalline precipitate was obtained. This was filtered off, washed with water, and dried; the yield of crude product was 13 grams (m. p. 91°), the theoretical yield being 14 grams. On recrystallisation from dilute alcohol it formed yellow needles, m. p. 95°, and proved to be identical with the benzenediazo-*p*-toluenesulphinate described in experiment I.

Action of o-Toluenediazonium Chloride on p-Toluenesulphonamide.

In this and the following experiments with *p*-toluenesulphonamide, 17 grams of the substance were dissolved in an alcoholic solution of 20 grams of potassium hydroxide, the alcohol was distilled off in a vacuum, and the residue dissolved in 150 c.c. of water. This process has the advantage that the bulk of the solution is smaller than in the previous experiments, and in spite of the large concentration of alkali the potassium salt of the sulphonamide does not separate out. *o*-Toluenediazonium chloride (made from 10.7 grams of *o*-toluidine) was then added, when a dark oil was formed. This was extracted with ether and purified as in experiment II. The yield of pure *o*-tolylazoimide was 10 grams (b. p. 90.5° at 31 mm.), the theoretical yield being 13.3 grams.

The aqueous solution was divided into two equal portions; one was treated with ferric chloride and the other with half the quantity of *o*-toluenediazonium chloride, as described in experiment II. The yield of ferric *p*-toluenesulphinate was 8 grams [Found : Fe = 10.6. $(\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2)_3\text{Fe}$ requires Fe = 10.74 per cent.]. The yield of the crude *o*-toluenediazo-*p*-toluenesulphinate (m. p. 74° with decomposition) was 11 grams, the theoretical yield being 13.7 grams. On recrystallisation from alcohol, it formed deep yellow needles and melted at 95° (Found : N = 10.26.

$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$
requires N = 10.22 per cent.).

Action of m-Toluenediazonium Chloride on p-Toluenesulphonamide.

The same quantities were used as in the previous experiment. The yield of pure *m*-tolylazoimide was 11 grams (b. p. 92.5° at 31 mm.), that of ferric *p*-toluenesulphinate 8.5 grams (Found: Fe = 10.65 per cent.), and that of the crude diazo-sulphinate (m. p. $62-66^{\circ}$) 11.5 grams. The last, on recrystallisation from alcohol, formed bright yellow needles, m. p. $72-73^{\circ}$ (Found: N = 10.16 per cent.).

Action of p-Toluenediazonium Chloride on p-Toluenesulphonamide.

The same quantities were used. The yield of pure *p*-tolylazoimide (b. p. 93° at 32 mm.) was 10 grams. It has a characteristic anisec smell. The yield of ferric *p*-toluenesulphinate was 8 grams (Found: Fe = 10.7 per cent.), and that of the crude diazo-sulphinate (m. p. $96-99^{\circ}$) was 12 grams. The latter, on recrystallisation from alcohol, formed bright yellow needles which melted at 100° with decomposition (Found: N = 10.59 per cent.).

Action of p-Chlorobenzenediazonium Chloride on p-Toluenesulphonamide.

The yellow, crystalline precipitate formed on the addition of *p*-chlorobenzenediazonium chloride (made from 12.7 grams of *p*-chloroaniline) to the solution of the sulphonamide decomposed very slowly with the separation of an oil. After remaining overnight, the mixture was extracted with ether and the extract purified as before. The yield of *p*-chlorophenylazoimide (b. p. $90-91^{\circ}$ at 15 mm.) was 8 grams, the calculated yield being 15 grams. The aqueous portion was divided into two equal parts and treated as before. The yield of ferric *p*-toluenesulphinate was 5 grams (Found: Fe = 10.67 per cent.), that of the crude *p*-chlorobenzenediazo-*p*-toluenesulphinate, m. p. $112-117^{\circ}$, was 8 grams, the calculated yield being 14.7 grams. The latter, on recrystallisation from alcohol, formed golden-yellow plates, m. p. 118° with decomposition (Found: N = 9.7 per cent. $\text{CH}_3\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ requires N = 9.5 per cent.).

Action of Benzenediazonium Chloride on Benzenesulphonamide.

In this and the following experiments 15.7 grams of the sulphonamide were dissolved in alcoholic potassium hydroxide, and the aqueous solution was prepared as before. Molecular quantities

of the various diazo-salts were used. With benzenediazonium chloride, the yield of pure phenylazoimide was 8 grams. The aqueous portion was also treated as before. The yield of ferric benzenesulphinate was 7 grams, the calculated yield being 8 grams (Found: Fe = 11.48. Calc., Fe = 11.69 per cent.). The free sulphinic acid obtained from it melted at 83–84° (Thomas gives m. p. 85°; *loc. cit.*).

The yield of the crude benzenediazobenzenesulphinate was 12 grams, the theoretical yield being 14.7 grams. On recrystallisation from dilute alcohol, it formed orange plates which melted at 75–76° with decomposition (Königs gives m. p. 75–76°; *loc. cit.*) (Found: C = 58.37; N = 11.8. Calc., C = 58.54; N = 11.38 per cent.). On reduction with zinc dust and acetic acid, it gave the dihydro-derivative, which, on recrystallisation from alcohol, formed colourless needles and melted at 158° (Königs gives m. p. 148°) (Found: N = 11.7. Calc., N = 11.3 per cent.).

Action of o-Toluenediazonium Chloride on Benzenesulphonamide.

The yield of pure *o*-tolylazoimide was 10 grams, that of ferric benzenesulphinate 6.5 grams (Found: Fe = 11.47 per cent.), and that of the crude *o*-toluenediazobenzenesulphinate 9.6 grams, the calculated yield being 13 grams. The last, on recrystallisation from alcohol, formed salmon-coloured, small prisms which melted with decomposition at 59–60° (Found: N = 10.6. $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{SO}_2\text{Ph}$ requires N = 10.77 per cent.).

Action of m-Toluenediazonium Chloride on Benzenesulphonamide.

The yield of pure *m*-tolylazoimide, b. p. 78° at 14 mm., was 9 grams, that of ferric benzenesulphinate 6.4 grams (Found: Fe = 11.48 per cent.), and that of the crude diazo-sulphinate 9.6 grams. The last, on recrystallisation from alcohol, formed yellow prisms which melted at 58° with decomposition (Found: N = 10.78 per cent.).

Action of p-Toluenediazonium Chloride on Benzenesulphonamide.

The yield of pure *p*-tolylazoimide was 9 grams, that of ferric benzenesulphinate 5.6 grams (Found: Fe = 11.48 per cent.), and that of the diazo-sulphinate 9.2 grams. The last, on recrystallisation from alcohol, formed golden-yellow prisms which melted at 85–86° with decomposition (Found: N = 10.8 per cent.); Hantzsch and Singer give m. p. 90° (*loc. cit.*).

Action of p-Chlorobenzenediazonium Chloride on Benzene-sulphonamide.

The yellow, crystalline diazoamine formed in this experiment appeared to be rather stable. After stirring for two hours, it was filtered, washed, and dried. It melted indefinitely at about 85° (Found: N = 14.41. $\text{SO}_2\text{Ph}\cdot\text{NH}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\text{Cl}$ requires N = 14.21 per cent.).

In another experiment, the reaction mixture was stirred for two days, when an oily liquid separated, which was extracted and purified in the usual way. The yield of pure *p*-chlorophenylazoimide was 7 grams. The aqueous portion was divided into two equal parts and treated as before. The yield of ferric benzenesulphinate was 5 grams, and that of the crude diazo-sulphinate 7 grams, the theoretical yield of the latter being 14 grams. On recrystallisation from alcohol, it formed deep yellow prisms, m. p. 106° with decomposition; Hantzsch and Singer give m. p. 102–103° (Found: N = 10.2. Calc., N = 9.98 per cent.).

In conclusion, we wish to express our thanks to Professor J. B. Cohen, F.R.S., for valuable criticism and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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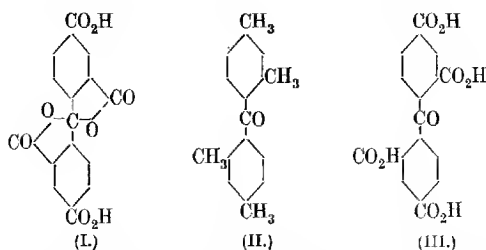
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CCXLII.—*The Optically Active Forms of the Keto-dilactone of Benzophenone-2 : 4 : 2' : 4'-tetracarboxylic Acid.*

By WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER.

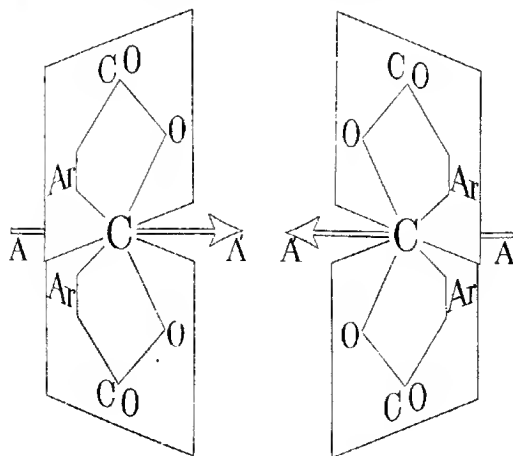
IN a preliminary communication (T., 1920, **117**, 1407) we described the resolution of the keto-dilactone of benzophenone-2 : 4 : 2' : 4'-tetracarboxylic acid (I) into optically active components, by which an experimental demonstration was given of a previously unrealised type of molecular asymmetry associated with *spirocyclic* constitution.*

* Leuchs and Gieseler have, however, shown (*Ber.*, 1912, **45**, 2114) that bis- δ -bromo- γ -valerolactone- $\alpha\alpha$ -spirane, which contains two similarly situated asymmetric carbon atoms as well as the spirane carbon atom, exists in three optically inactive forms.



Like methylcyclohexylideneacetic acid (Perkin, Pope, and Wallach, T., 1909, **95**, 1789), 4-oximinocyclohexanecarboxylic acid (Mills and Bain, T., 1910, **97**, 1866), *d*- and *l*-inositol (Maquenne, *Ann. Chim. Phys.*, 1893, [vi], **29**, 271; Tanret, *Compt. rend.*, 1899, **109**, 908) and triethylenediaminecobaltic bromide (Werner, *Ber.*, 1912, **45**, 121) and certain analogous co-ordination compounds, this substance affords an example of an optically active compound which contains no asymmetric atom in the ordinary sense.

As regards its chemical structure, the compound is highly symmetrical; the molecule is divisible at the central spirane carbon atom into two identical halves. The molecular asymmetry is due to the fact that these two halves lie in planes which intersect—according to the theory of van't Hoff, at right angles—so that the molecule possesses as its sole element of symmetry a binary axis of the first order AA' and is therefore non-superposable on its mirror image (in the diagram *Ar* represents the aromatic residue $C_6H_3 \cdot CO_2H$).



The relationship between the two enantiomorphous forms is somewhat similar to that between a right-handed, two-bladed screw propeller and its left-handed analogue.

Benzophenonetetracarboxylic acid (Mills, *Proc. Camb. Phil. Soc.*, 1915, **18**, 149), from which the active keto-dilactonic acids are derived, was obtained by the oxidation of di-*m*-xylyl ketone. Since the latter compound was prepared by the condensation of *m*-xylene with carbonyl chloride, there can be little doubt that it possesses the formula II, and therefore that benzophenonetetracarboxylic acid and its keto-dilactone have the constitutions III and I. An experimental proof of the correctness of these formulæ is given below.

The oxidation of the ketone was carried out in two stages. By prolonged boiling with dilute nitric acid a mixture of acids was obtained which apparently consisted chiefly of dibasic acids. These were then oxidised to the tetrabasic acid with potassium permanganate. The conversion of the easily soluble tetrabasic acid into its sparingly soluble keto-dilactone was readily effected by heating with hydrochloric acid. The keto-dilactonic acid melts at 400°.

We have now carried out the resolution of the keto-dilactonic acid with considerably larger quantities of material than before, and have obtained both the dextro- and the lævo-form in what we believe to be a state of optical purity. Phenylethylamine was again employed for the resolution. The enantiomeric forms of this substance are probably the most readily accessible of the synthetic optically active bases (Lovén, *J. pr. Chem.*, 1905, [ii], **72**, 307), and may prove of service for the resolution of acids in many other cases where the natural alkaloids fail. To obtain the *d*-acid, the inactive acid was combined in the cold with the equivalent quantity of the *l*-base under such conditions that a little more than half the total quantity of salt crystallised. This was decomposed in the cold with hydrochloric acid, and the liberated acid was combined again in the same way with more *l*-base, and the process was repeated seven times. This method was employed because it involved no elevation of temperature, for the lactone rings are rather readily opened.

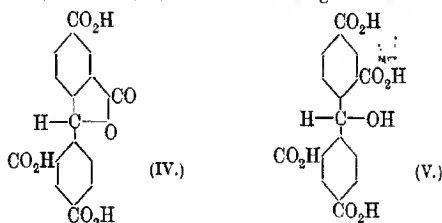
The *l*-acid was isolated by combining the inactive acid with *d*-phenylethylamine and recrystallising the salt repeatedly from methyl alcohol and ether until it gave an acid of constant specific rotation. In spite of the warming required this method of resolution is at least as effective as the other.

The specific rotation of the active keto-dilactonic acids in methyl ethyl ketone solution was found to be comparatively low and to vary considerably with the concentration, being greater in more

concentrated solutions. For the *d*-acid was found $[\alpha]_D^{19.5^\circ}$ at a concentration of 7.76 grams per 100 c.c., and for the *l*-acid at the same concentration (by interpolation) $[\alpha]_D - 19.53^\circ$. It has already been stated (T., 1920, 117, 1409) that the solubility of the optically active modifications in methyl ethyl ketone is much greater than that of the inactive acid, as is strikingly shown by the abundant precipitate of the inactive acid which is immediately formed when strong solutions of the *d*- and *l*-acids are mixed. This shows that the inactive acid is a racemic substance. The *l*-acid melts at 407° . The melting point of the active form is thus 2° lower than that of the racemic acid.

Treatment of the compound with excess of alkali very rapidly opens the keto-dilactonic rings, and in consequence the rotatory power of the active modifications disappears completely when they are dissolved in sodium hydroxide solution. Even in the presence of sodium hydrogen carbonate the rotatory power gradually falls to zero. The specific rotation of the sodium salt in aqueous solution is in the opposite sense to that of the free keto-dilactonic acid in methyl ethyl ketone and has a much smaller value.

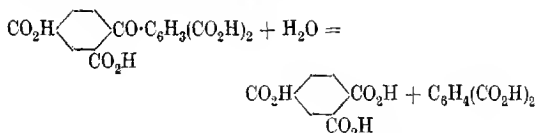
We have also resolved the lactone of benzhydrol-2:4:2':4'-tetracarboxylic acid (IV) and have investigated its oxidation to



find whether the optically active keto-dilactonic acid could be produced in this manner. The inactive lactonic acid was obtained by dissolving the keto-dilactonic acid in excess of ammonia and reducing with zinc dust. The benzhydroltetracarboxylic acid thus produced is transformed into its lactone with the greatest readiness when set free from its salts. The lactonic acid was resolved by means of brucine. From an alcoholic solution of equivalent quantities of the acid and brucine the brucine salt of the *l*-acid crystallised out very slowly, and on decomposition gave an acid showing the specific rotation $[\alpha]_D - 258^\circ$ in methyl ethyl ketone solution. The specific rotation of this compound, which contains an ordinary asymmetric carbon atom, is thus very much higher than that of the chemically closely related but centro-symmetric keto-dilactonic acid.

It was found that the oxidation to the keto-dilactonic acid could be effected by chromic acid in glacial acetic acid solution. However, the product obtained from the optically active lactonic acid proved to be inactive. This is not surprising, for since the reaction involves the oxidation of a hydrogen atom attached to the asymmetric carbon atom, the change would be expected to be associated with much racemisation.

The optically active lactonic acid loses its activity completely when dissolved in excess of sodium hydroxide solution, showing that when the lactone ring is opened the central carbon atom ceases to be asymmetric. This fact is important, because it allows the conclusion to be drawn that in benzhydroltetracarboxylic acid (V), and consequently also in benzophenonetetracarboxylic acid, the two residues, $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_2$, are alike; and when this is established the constitution of the two acids becomes comparatively easy to determine. For when benzophenonetetracarboxylic acid is fused with sodium hydroxide, it undergoes hydrolysis, giving a mixture of two acids. The less soluble of these was readily identified as isophthalic acid. The more soluble had the composition of a benzenetricarboxylic acid, $\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$, and when heated gave an anhydride, $\text{C}_6\text{H}_3(\text{C}_2\text{O}_3)\cdot\text{CO}_2\text{H}$. It was therefore either hemimellitic or trimellitic acid. The melting point of the acid was $228\text{--}230^\circ$ and of the anhydride $159\text{--}162^\circ$. These are the melting points of trimellitic acid and of its anhydride.* The more soluble acid was accordingly trimellitic acid. Hence the hydrolysis must proceed in accordance with the equation:



for, since benzophenonetetracarboxylic acid was prepared from *m*-xylene, the two carboxyl groups attached to each nucleus in the molecule of this acid must be in the *meta*-position to one another.

The constitution of one half of the molecule is thus fixed and, since the two halves have been shown to be alike, the constitution II assigned to the acid is therefore established.

EXPERIMENTAL.

Di-m-xylol Ketone.—The preparation of a dixylol ketone by leading carbonyl chloride into cooled "xylol" and treating the

* Hemimellitic acid melts at 190° and its anhydride at 196° .

solution with aluminium chloride was briefly described by Ador and Rilliet (*Ber.*, 1878, **11**, 399); we have, however, been able to find no record in the literature of the preparation of pure di-*m*-xylyl ketone. It can be readily obtained in the following manner. Liquid carbonyl chloride (14.25 c.c.) is allowed to evaporate slowly into a mixture of *m*-xylene (50 grams), carbon disulphide (120 c.c.), and aluminium chloride (63 grams) cooled in ice. The greater part of the aluminium chloride dissolves and the liquid separates into two layers, the lower of which is dark coloured and contains the aluminium chloride compound of the ketone. After forty-eight hours, the mixture is poured on to ice. The aqueous layer is separated, the lower layer, which consists of a carbon disulphide solution of the product, is added to dilute hydrochloric acid, and a current of steam is led in to remove the carbon disulphide and unchanged *m*-xylene and decompose traces of xyloyl chloride. The crude ketone which remains is dissolved in ether and after washing with alkali, drying, and removal of the ether, is distilled under diminished pressure. At 17 mm. nearly the whole distils at 200–201° (Found : C = 85.6; H = 7.7. $C_{17}H_{18}O$ requires C = 8.7; H = 7.5 per cent.). The yield of pure ketone is about 70 per cent. of the *m*-xylene taken.

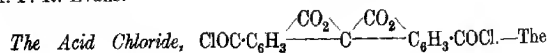
Keto-dilactone of Benzophenone-2 : 4 : 2' : 4'-tetracarboxylic Acid.—The ketone (10 grams) was boiled with dilute nitric acid (120 c.c.) obtained by mixing the concentrated acid (*d* 1.42) with 6 volumes of water. The boiling was continued until the greater part of the oil had become soluble in aqueous sodium carbonate solution. The rate of oxidation varied considerably in different experiments, but usually two to three days' boiling was required. The product was a faintly yellow oil which solidified on cooling. It was dissolved in ether and the acids which had been formed were extracted from the ethereal solution with aqueous sodium carbonate solution. These contained a certain amount of nitro-acids which it was essential to remove. This was done by reduction with ferrous hydroxide. A solution of the acids in an excess of sodium hydroxide was added to a solution of ferrous sulphate, containing 10 grams of the crystallised salt for the acids from each 10 grams of ketone, and the mixture was digested for five hours on the water-bath. After cooling, it was acidified with hydrochloric acid and the precipitated acids were taken up in ether. On titration of the acids thus obtained, the volume of normal alkali required to neutralise 1 gram was found to range from 6.22 c.c. to 7.22 c.c., the average being 6.8 c.c. For 1 gram of an acid formed by the conversion of two of the methyl groups of dixylyl ketone into carboxyl groups the volume of normal alkali required would be 6.71 c.c. It would appear, therefore,

that the oxidation with dilute nitric acid leads to the formation chiefly of such dihasic acids.

As the product was presumably a mixture, it was not further investigated, but was at once oxidised to the tetrabasic acid with potassium permanganate. From the alkali equivalent the quantity of permanganate required for the oxidation was calculated, and an amount 10 per cent. in excess of this was added in 5 per cent. solution to the boiling solution of the acids in potassium hydroxide. The permanganate was added in small quantities until decolorisation became slow. The remainder was then added all at once and the mixture gently boiled for six hours. The tetrabasic acid is a comparatively soluble compound which is precipitated by hydrochloric acid as a viscid oil from not too weak solutions of its salts. Addition of excess of hydrochloric acid salts out more of the acid, but the precipitate dissolves again on warming. If this solution is now heated to boiling, the keto-dilactonic acid separates gradually as a colourless, dense, crystalline powder. The filtrate from the manganese dioxide was therefore concentrated, strongly acidified with hydrochloric acid, and heated on the water-bath until the separation of the keto-dilactonic acid was complete. The yield is fairly satisfactory. For example, in one series of experiments, 30 grams of the keto-dilactonic acid were obtained from 34 grams of dixylyl ketone.

The compound is exceedingly sparingly soluble in most of the common solvents, acetone and methyl ethyl ketone being those by which it is most readily dissolved. Small quantities can be recrystallised from boiling glacial acetic acid. The melting point observed with a mercury thermometer immersed to the zero mark in a bath of mixed sodium and potassium nitrates was 390° . The corrected value is 409° (Found: C = 59.8; H = 2.5. $C_{17}H_8O_8$ requires C = 60.0; H = 2.4 per cent.). The compound dissolves in cold sodium hydrogen carbonate solution without the lactone rings being opened to any great extent, and is immediately reprecipitated when the solution is acidified. If the solution in sodium hydrogen carbonate, however, has been boiled, or if the substance has been dissolved in sodium hydroxide solution, the lactone rings are opened and on acidification no precipitate, or in stronger solutions an amorphous precipitate of the tetrabasic acid, is obtained.

The following derivatives of the keto-dilactonic acid illustrate the stability of the keto-dilactonic group. For assistance with the preparation and investigation of these our thanks are due to Mr. A. F. R. Evans.



keto-dilactonic acid (15 grams) was moistened with phosphoryl chloride and heated for three hours at 100–120° with phosphorus pentachloride (19.2 grams). The phosphoryl chloride was removed by distillation under diminished pressure, and the residue crystallised from toluene. The compound consists of colourless needles melting at 187° (Found: Cl = 18.86. $C_{17}H_8O_6Cl_2$ requires Cl = 18.83 per cent.).

The Ethyl Ester, $CO_2Et \cdot C_6H_3 \begin{smallmatrix} \diagup CO_2 \\ \diagdown \end{smallmatrix} C \begin{smallmatrix} \diagup CO_2 \\ \diagdown \end{smallmatrix} C_6H_3 \cdot CO_2Et$.—A solution of the acid chloride in benzene was heated with excess of absolute alcohol. The ester was deposited on cooling, and after recrystallisation from alcohol and benzene melted at 215–217°. It is rather sparingly soluble in hot alcohol or acetone; it dissolves much more readily in benzene (Found: C = 63.7; H = 4.0. $C_{21}H_{16}O_8$ requires C = 63.6; H = 4.0 per cent.).

Resolution of the Keto-dilactonic Acid.

The d-Keto-dilactonic Acid.—The keto-dilactonic acid (8.43 grams) was suspended in methyl alcohol (100 c.c.) and a solution of *l*- α -phenylethylamine (6.0 grams), of specific rotation $[\alpha]_D^{25} = -40.4^\circ$, in methyl alcohol (5 c.c.) was added drop by drop. When all the base had been introduced, dry ether (105 c.c.) was added. After stirring for ten minutes, the crystalline salt was collected. It weighed 8.5 grams. The keto-dilactonic acid was then liberated by digesting with dilute hydrochloric acid (*d* 1.08). After careful washing with water, it was dried, and weighed 4.9 grams. This acid was again combined with the *l*-base as before and the whole process was repeated a number of times. After the fourth salt-formation the keto-dilactonic acid gave the following data when polarimetrically examined in methyl ethyl ketone solution; 1.617 grams in 13.1 c.c. gave $\alpha_D^{25} + 4.55^\circ$ (*l* = 2), whence $[\alpha]_D^{25} + 18.4^\circ$. After a fifth salt-formation, 1.0153 grams in 13.1 c.c. gave $\alpha_D^{25} + 2.95^\circ$ (*l* = 2), whence $[\alpha]_D^{25} + 19.03^\circ$. After the acid had been subjected to a seventh salt-formation, the salt was recrystallised from hot methyl alcohol with subsequent addition of ether. The liberated acid (0.5181 gram) in 6.68 c.c. of methyl ethyl ketone gave $\alpha_D^{25} + 1.51^\circ$ (*l* = 1), whence $[\alpha]_D^{25} + 19.5^\circ$. This value agrees with that of the optically pure *l*-acid.

The l-Keto-dilactonic Acid.—The keto-dilactonic acid (18.4 grams) was suspended in methyl alcohol (180 c.c.) and a solution of *d*- α -phenylethylamine (13.1 grams), of specific rotation $[\alpha]_D^{25} + 40.4^\circ$, in methyl alcohol (20 c.c.) was added drop by drop. After all the base had been introduced, anhydrous ether (160 c.c.) was added.

Stirring was continued for fifteen minutes. The salt thus obtained (16.6 grams) was recrystallised from methyl alcohol (350 c.c.) and ether (550 c.c.). The weight of the recrystallised salt was 7.0 grams. After two further recrystallisations from methyl alcohol and ether, 4.8 grams of salt were obtained. Of this 1.8 grams were decomposed with dilute hydrochloric acid and the resulting acid was examined in the polarimeter; 1.05 grams in 13.1 c.c. of methyl ethyl ketone gave $\alpha_D^{15} - 3.15^\circ$ ($l = 2$), whence $[\alpha]_D^{15} - 19.65^\circ$. The remainder of the salt (3 grams) was again crystallised from methyl alcohol (80 c.c.) and ether (200 c.c.). Of the resulting 2.4 grams, 1.9 grams were decomposed. The acid obtained (1.05 grams) in 13.1 c.c. of methyl ethyl ketone gave $\alpha_D^{15} - 3.15^\circ$ ($l = 2$), whence $[\alpha]_D^{15} - 19.65^\circ$. A fourth recrystallisation of the salt had failed therefore to produce any further rise in optical rotatory power, and it was concluded that the optically pure *l*-acid had been obtained.

The specific rotation in methyl ethyl ketone solution varies considerably with the concentration. This is shown by the following observations on the pure *l*-acid.

1.48 grams in 13.1 c.c. gave $\alpha_D^{15} - 4.62^\circ$ ($l = 2$),

whence $[\alpha]_D^{15} - 20.44^\circ$.

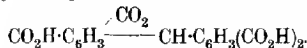
0.45 gram in 13.1 c.c. gave $\alpha_D^{15} - 1.22^\circ$ ($l = 2$),

whence $[\alpha]_D^{15} - 17.76^\circ$.

The *l*-acid melts at 407° (corrected).

Action of Sodium Hydrogen Carbonate.—The effect of a solution of sodium hydrogen carbonate on the active acid was examined in order to investigate the stability of the keto-dilactonic rings towards this reagent. The pure *levo*-acid (0.452 gram) was dissolved in a solution of sodium hydrogen carbonate (0.82 gram, that is, rather more than three and a half times the equivalent quantity) and the solution was diluted to a volume of 13.1 c.c. and examined in the polarimeter as rapidly as possible. The observed rotation was $\alpha_D^{15} + 0.18^\circ$ ($l = 2$). Thus the *l*-acid gave a dextrorotatory sodium salt. After one hour, the same solution showed $\alpha_D^{15} + 0.10^\circ$ ($l = 2$). After eighteen hours, the activity had disappeared.

Lactone of Benzhydrol-2 : 4 : 2' : 4'-tetracarboxylic Acid.



This compound was prepared by reducing the keto-dilactonic acid with zinc dust and ammonia. The keto-dilactonic acid (4 grams) was dissolved in aqueous ammonia, *d* 0.88 (40 c.c.), and zinc

dust (12 grams) was added in three portions at intervals of twenty minutes while the mixture was heated on the water-bath. The precipitate obtained by acidifying the filtrate from the excess of zinc dust was crystallised from 60 per cent. acetic acid. The keto-dilactonic acid can also be readily reduced to the lactonic acid by suspending it in 50 per cent. acetic acid and heating with excess of zinc dust. The lactonic acid crystallises in slender needles melting at $309-311^{\circ}$ (Found: C = 59.4; H = 3.1. $C_{17}H_{10}O_8$ requires C = 59.6; H = 2.9 per cent.). When a solution of the lactonic acid in aqueous sodium hydroxide solution is acidified with dilute sulphuric acid, no precipitate appears at first; after a short time, however, a gradual deposition of the lactonic acid begins, the separation being greatly accelerated by heating the solution.

Resolution of the Lactonic Acid.—The acid (5.13 grams) and anhydrous brucine (7 grams) were dissolved in rectified spirit (1200 c.c.) and the solution was inoculated with crystals of the salt which had been obtained previously. The liquid was allowed to evaporate slowly for six weeks; its volume had then become reduced to about one half and a crop of crystals of brucine salt had been deposited. By decomposition of this salt with dilute hydrochloric acid (*d* 1.08) and careful removal of the brucine, 2.65 grams of lactonic acid were obtained, which proved to be strongly levorotatory.

0.3046 Gram in 13.1 c.c. of methylethyl ketone gave $\alpha_D^{25} = -11.97^{\circ}$ ($l = 2$), whence $[\alpha]_D^{25} = -258^{\circ}$.

0.2 Gram in 30 c.c. of acetone gave $\alpha_D^{25} = -6.13^{\circ}$ ($l = 4$), whence $[\alpha]_D^{25} = -229.9^{\circ}$.

This *l*-acid (0.3 gram) was dissolved in dilute aqueous sodium hydroxide solution (13.1 c.c.) and examined in the polarimeter. No trace of optical activity could be observed. The *l*-lactonic acid is much more soluble in alcohol than the inactive form. It crystallises from 50 per cent. alcohol in hemispherical aggregates of small needles. The acid recovered from the mother-liquor from which the brucine salt had crystallised showed a small dextrorotation.

Fusion of the Keto-dilactonic Acid with Potassium Hydroxide.

The keto-dilactonic acid (3 grams) was dissolved in a little aqueous potassium hydroxide solution, and added to solid potassium hydroxide (40 grams), and the mixture was heated at $280-285^{\circ}$ for three hours. When cold, the melt was dissolved in water, dilute sulphuric acid was added so as to leave the liquid slightly alkaline, and the precipitated potassium sulphate was removed. The filtrate was then acidified, when a sparingly soluble acid was precipitated, the weight of which, after recrystallisation from dilute

alcohol, was 1.1 grams. This was shown to be isophthalic acid. After purification by distillation and further recrystallisation, it melted at 324° (uncorr.), and a specimen of pure isophthalic acid prepared by the oxidation of *m*-xylene, as well as a mixture of the two preparations, melted at the same temperature. The equivalent was found to be 83.8 (calc., 83). The methyl ester, prepared by heating the acid with methyl alcohol and sulphuric acid, melted at 62.5° (the ester apparently contained a trace of a less soluble impurity and the melting point was not raised by repeated crystallisation). The melting point of a mixture of this ester with pure methyl isophthalate, which melts at 63–64°, was 62.5°.

Trimellitic Acid.—The filtrate from the crude isophthalic acid was saturated with ammonium sulphate and extracted three times with ether. By evaporation of the ether an acid was obtained which was readily soluble in water. To separate from traces of isophthalic acid this was converted into its barium salt (barium isophthalate is easily soluble in water) by heating its solution in dilute ammonia with barium chloride. The barium salt was slowly deposited from the hot solution. It was collected, redissolved in dilute hydrochloric acid, and reprecipitated by heating after neutralising with ammonia. The acid was isolated from the barium salt by dissolving in hydrochloric acid and extracting with ether. The acid thus obtained weighed 0.85 gram, the purification through the barium salt being attended with considerable loss. It was recrystallised by dissolving in hot water (3 c.c.) and adding concentrated hydrochloric acid (4.5 c.c.) (Found: C = 51.24; H = 3.1. Calc., C = 51.4; H = 2.9 per cent.).

The acid melted at 228–230°. Ekstrand gives 228° as the melting point of trimellitic acid (*J. pr. Chem.*, 1891, [ii], 43, 429), Baeyer (*Ber.*, 1899, 32, 2445) gives 224–225°.

Trimellitic Anhydride.—The acid was heated in a bath at 210–220° under diminished pressure (2 mm.), when the anhydride sublimed (Found: C = 56.0; H = 2.2. Calc., C = 56.25; H = 2.0 per cent.). It melted at 159–162°. Baeyer (*Annalen*, 1873, 166, 341) gives 157–158° as the melting point of trimellitic anhydride, and Schultze (*Annalen*, 1908, 359, 142) gives 162.5–163.5°.

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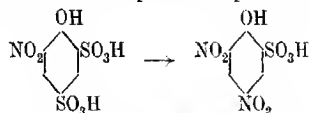
CCXLIII.—*Production of Picric Acid from the Sulphonic Acids of Phenol.*

By RUTH KING.

THE preparation of picric acid from phenol by the successive action of sulphuric and nitric acids has engaged a considerable amount of attention. Since better yields of picric acid are usually produced when an amount of sulphuric acid is employed sufficient to give a very considerable proportion of phenol-2:4-disulphonic acid, the view that the formation of this acid is necessary before proceeding to nitration has been accepted in many quarters as correct.

That the certainty of a good yield is increased by the disulphonation of phenol has been confirmed by Marquoyrol, Carré, and Loriette (*Bull. Soc. chim.*, 1920, [iv], 27, 143), but the fact remains that in some manufacturing processes good yields are obtained from mixtures containing a considerable amount of phenol-4-sulphonic acid, so that evidently high sulphonation is not the only factor which comes into play. Phenol-4-sulphonic acid can give yields up to 79 per cent. of the theoretical, if nitrated in presence of a large excess of concentrated sulphuric acid, whilst 2-nitrophenol-4-sulphonic acid will give a yield up to 83 per cent. of that theoretically obtainable if nitrated in presence of sufficient sulphuric acid.

In the case of phenol-2:4-disulphonic acid, nitrolysis of the *p*-sulpho-group is preferred; if 6-nitrophenol-2:4-disulphonic acid is subjected to nitrolysis, the sulpho-group in position 4 is preferentially replaced and 4:6-dinitrophenol-2-sulphonic acid first formed.



This result is complementary to that of Marquoyrol, Carré, and Loriette (*loc. cit.*), who found that picric acid is produced more rapidly from 2:6-dinitrophenol-4-sulphonic acid than from the isomeric 2:4-dinitrophenol-6-sulphonic acid. The present author has also obtained excellent yields of picric acid by the nitrolysis of 2:6-dinitrophenol-4-sulphonic acid, a very small amount of oxalic acid being produced at the same time. 2-Nitrophenol-4-sulphonic acid gives more oxalic acid under the same conditions; even greater amounts are formed from phenol-4-sulphonic acid, but the quantity obtained is dependent largely on the concentration of the sulphuric acid; the greater this is, the smaller is the quantity of oxalic acid produced.

To obviate formation of oxalic acid and dinitrophenol, the latter of which shows great resistance to further nitration by diluted acids, it is essential to monosulphonate the phenol in position 4, and desirable to introduce a second sulfo-group in position 2, or, alternatively, to nitrate the phenol-4-sulphonic acid in presence of a considerable excess of sulphuric acid. Phenol-2 : 4 : 6-trisulphonic acid is prepared only by very drastic sulphonation; the amount in an ordinary sulphonation mixture is consequently negligible.

In studying the manufacture of picric acid from phenol by the usual process of successive sulphonation, dilution, and nitration, the following facts must be considered.

1. The sulphonation mixture consists almost entirely of phenol-4-sulphonic acid, phenol-2 : 4-disulphonic acid, and an excess of concentrated sulphuric acid.

2. When nitric acid acts on a phenolsulphonic acid in presence of excess of concentrated sulphuric acid, hydrogen of the nucleus is replaced by the nitro-group.

3. In presence of dilute sulphuric acid, sulfo-groups are replaced by the nitro-group.

4. In dilute acid solution, nitric acid exerts an oxidising action resulting in the formation of oxalic acid; this is the more marked as the phenol nucleus is less protected by substituents.

The author bases the views expressed above on a study of the action of diluted nitric acid in presence of sulphuric acid on the following compounds.

- (a) Phenol-4-sulphonic acid.
- (b) Phenol-2 : 4-disulphonic acid.
- (c) 2-Nitrophenol-4-sulphonic acid.
- (d) 4-Nitrophenol-2-sulphonic acid.
- (e) 2 : 6-Dinitrophenol-4-sulphonic acid.
- (f) 4 : 6-Dinitrophenol-2-sulphonic acid.
- (g) 6-Nitrophenol-2 : 4-disulphonic acid.

Since the formation of phenol-2-sulphonic acid, phenol-2 : 6-disulphonic acid and phenol-2 : 4 : 6-trisulphonic acid in the sulphonation mixture is negligible, neither their nitration nor that of 4-nitrophenol-2 : 6-disulphonic acid has been studied.

EXPERIMENTAL.

(a) *Phenol-4-sulphonic Acid.*

This acid (Kekulé, *Zeitsch. Chem.*, 1867, 199; *Ber.*, 1869, 2, 330; Post, *Annalen*, 1880, 205, 64) was used in the form of its pure

crystallised sodium salt; the formula assigned to it by Shadwell (*Jahresb.*, 1881, 874) was controlled (Found: $\text{H}_2\text{O} = 15.8$; $\text{Na} = 11.4$. $\text{C}_6\text{H}_5\text{O}_4\text{SNa} \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 15.5$; $\text{Na} = 11.7$ per cent.).

Weighed amounts of the salt, sulphuric acid, and water were treated with a known amount of nitric acid, the latter being added slowly, as the reaction is apt to be violent when much sulphuric acid is present.

All the solutions turned red. They were cooled and kept overnight. By next morning all had retained their red colour, whilst a reddish-brown solid floated on the surface, with the exception of mixtures 1 and 2 (see below), in which a yellow solid had also been deposited.

The mixtures were then heated for eight hours at 100° ; oil separated in mixtures 4, 5, 6, and 7, this separation being more marked and disappearing more slowly the lower the concentration of the sulphuric acid. It was noticed that, after cooling, mixtures 1 and 2 retained a red tint, whilst mixtures 4, 5, 6, and 7 were pale yellow, this tint decreasing regularly as the ratio of water to sulphuric acid increased.

The picric acid was filtered off, washed with 60 c.c. of water, dried to constant weight at 75° , and weighed, and the melting point was determined.

No further yield of picric acid was obtained by after-nitration of the filtrate with 7 c.c. of nitric acid of 67 per cent.

Expt.	Sodium salt (0.1 mol.). Grams.	Sulphuric acid (95 per cent.). Grams.	Water. Grams.	Nitric acid (67 per cent.; 0.4 mol.). Grams.	Yield. Grams.	Yield per cent.	M. p.
1	23.2	59.6	0	39.9	18.1	79	120-121°
2	"	60.9	10	39.1	17.4	78	120
3	"	61.1	20	40.3	17.6	77	120
4	"	50.8	30	39.1	17.7	77.3	120
5	"	38.6	40	40.5	17.7	77.3	118-120
6	"	30	50	40	16.7	73	100-113
7	"	20	60	40	16.1	70.3	below 92

Separate experiments showed that more oxalic acid was produced in presence of dilute than of concentrated sulphuric acid.

(b) *Phenol-2:4-disulphonic Acid.*

The free acid is deliquescent (Griess, *Annalen*, 1866, 137, 69; Kekulé, *Zeitsch. Chem.*, 1866, 693), but well-crystallised barium (Zingel, *Jahresb.*, 1885, 1597) and sodium salts exist. Zingel describes the barium salt as crystallising with 4 molecules of water.

The metal content was checked in an anhydrous specimen (Found : Ba = 34.2. Calc., Ba = 35.2 per cent.).

The Sodium Salt.—Direct preparation of this salt from a sulphonation mixture is usually an uncertain operation, but the following method gave good results : one hundred grams of phenol and 400 grams of oleum (23 per cent.) were heated at 100° for three and a half hours and poured into a solution of 450 grams of sodium sulphate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) in 500 c.c. of water at 32°. On the next day, the crystalline precipitate was collected, washed with a little water, and dried in the air.

The product had a slightly brown tinge and weighed 200 grams; the weight of the anhydrous product, dried at 120°, was 180 grams (about 57 per cent. of the theoretical) (Found : Na = 14.97. Calc., Na = 15.43 per cent.).

In several preparations, a colloidal mass was obtained in place of the well-defined crystals referred to above. The salt, when collected and dried, always gave results too low in sodium (Found : in different preparations, Na = 14.9, 13.6, 14.6 per cent.).

Such results would be obtained if the phenoldisulphonic acid had condensed with itself to give a diphenolsulphonetrisulphonic acid, but sulphur estimations to confirm this supposition have not been carried out.

That phenol-2:4-disulphonic acid gives good yields of picric acid remarkably free from dinitrophenol, has been established by other workers (private communication from Dr. Clarence Smith; Marquetryol, Carré, and Lorient, *loc. cit.*).

(c) 2-Nitrophenol-4-sulphonic Acid.

This acid has been previously described as crystallising with $3\text{H}_2\text{O}$. Hydrated, it is said to melt at 51.5°; in the anhydrous condition, at 122°. It has been prepared by sulphonation of o-nitrophenol with fuming sulphuric acid (Kekulé, *Zeitsch. Chem.*, 1867, 64) and with chlorosulphonic acid (Armstrong, *ibid.*, 1871, 321; Mazurowska, *J. pr. Chem.*, 1876, [ii], 13, 171), or by nitrating phenol-4-sulphonic acid (Kolbe and Graube, *Annalen*, 1868, 147, 71; Kekulé, *Ber.*, 1868, 2, 332; Korner, *Jahresb.*, 1872, 605). It is also obtained by the action of potassium hydroxide on 1-bromo-2-nitrobenzene-4-sulphonic acid (Goslich, *Annalen*, 1876, 180, 105) and on 2-nitroaniline-4-sulphonic acid (Nietzki and Lerch, *Ber.*, 1888, 21, 3221).

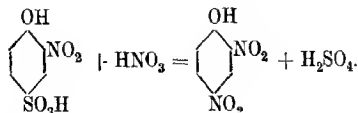
The Sodium Salt.—This was very readily prepared by the following method : 120 grams of crystallised sodium phenol-4-sulphonate dissolved in 300 c.c. of hot water were treated with 72 c.c. of nitric

acid (d 1.4) in the course of fifteen to twenty minutes, the temperature during nitration being kept at about 60° . The reaction proceeded quite smoothly and was accompanied by slight fuming, especially towards the end of the reaction. On cooling, an orange, crystalline salt separated. In one experiment, supersaturation was very noticeable. The salt was collected and washed with a little water; the crystals became paler in colour on drying. One hundred and twenty grams of the *p*-sulphonate gave 128 grams of sodium 2-nitrophenol-4-sulphonate (about 83 per cent. of the theoretical yield). After recrystallisation, the following figures were obtained on analysis (Found: $H_2O = 18.7$; $Na = 9.50$. $C_6H_4O_5NSNa, 3H_2O$ requires $H_2O = 18.7$; $Na = 9.55$ per cent.).

In the preparation described, nearly two molecular proportions of nitric acid were employed for one of sodium phenolsulphonate. With a lower proportion of nitric acid (140 c.c.) to the phenolsulphonate (300 grams), the yield was seriously reduced (150 grams). A further quantity was recovered by evaporation, but in an impure condition. On the other hand, attempts to increase the yield by the addition of more nitric acid after the first separation of salt led to the formation of 2:4-dinitrophenol, so that it is obviously advisable to cool well and to recover as much of the nitrosulphonate as possible in the first instance.

In an actual experiment in which 172.8 grams of the nitrosulphonate were obtained from 250 grams of sodium phenolsulphonate, an attempt was made to recover more of the nitrosulphonate by adding a further 10 c.c. of nitric acid (d 1.4) to the filtrate and warming until fumes ceased to be evolved. A yellow solid separated on cooling, which was very slightly soluble in cold water and after recrystallisation from boiling water melted at $112-113^{\circ}$. The melting point of the mixture with an authentic specimen of 2:4-dinitrophenol proved the identity of the compound, of which 20 grams were obtained.

It is evident that the sodium 2-nitrophenol-4-sulphonate in the solution underwent nitrolysis by the treatment, according to the equation:



As will be seen later, 2:6-dinitrophenol-4-sulphonic acid may be obtained as the chief product of the reaction between 2-nitrophenol-4-sulphonic acid and dilute nitric acid, provided that an excess of sulphuric acid is present.

The Barium Salt.—This was prepared by precipitating the solution of the sodium salt with barium chloride; Kekulé's formula, $(C_6H_4O_6NS)_2Ba.H_2O$, was confirmed.

The Free Acid.—This is described in the literature as crystallising with three molecules of water. A convenient method of preparation is to dissolve the barium salt (which can readily be obtained in a state of purity) in hot water, precipitate with the calculated amount of dilute sulphuric acid, remove the barium sulphate, and evaporate the filtrate. The residue is dissolved in a small quantity of water, filtered from any residual barium sulphate, and again concentrated. Care has to be taken in concentrating, as the acid is very soluble in water, and in the hydrated condition melts at 49° (given as 51.5° in the literature). The hydrated acid forms long, pale yellow needles and dissolves in water with very marked absorption of heat. Titration (with phenolphthalein as the indicator) gave a molecular weight of 268; $NO_2.C_6H_3(OH).SO_3H.H_2O$ requires $M = 272$. The end-point was difficult to determine on account of the colour of the sodium salt of the acid.

Whilst phenol-4-sulphonic acid gives poor yields of picric acid of inferior quality when nitrated in presence of much water and little sulphuric acid, 2-nitrophenol-4-sulphonic acid gives much better results under the same conditions. In the following table, the results are given of the nitration of sodium 2-nitrophenol-4-sulphonate ($+3H_2O$), the amounts of water and sulphuric acid being varied. The procedure adopted was that described for sodium phenol-4-sulphonate.

Nitration of 2-Nitrophenol-4-sulphonic Acid.

(Heating at 100° for eight hours.)

Expt.	Sodium salt (0.1 mol.). Grams.	Sulphuric acid (94 per cent.). Grams.	Water. Grams.	Nitric acid (67 per cent.; 0.32 mol.). Grams.	Yield. Grams.	Yield per cent.	M. p.
1	29.5	61.2	0	30	18.5	80.8	121°
2	"	59.1	10	33.9	—	—	—
3	"	60.5	20	30.4	17.85	78	120
4	"	50.7	30	30.6	18.2	79.5	119-120
5	"	44.8	40	29.5	19.1	83.5	120-121
6	"	30	50	30	18.95	82.6	119-120
7	"	20	60	30	18.05	78.8	118-119.5

Comparison of experiments 6 and 7 of the two series shows very plainly the great improvement effected during nitrating in presence of small amounts of sulphuric acid when the molecule of the phenolsulphonate has been stabilised by the introduction of the

nitro-group. In this connexion, a pair of comparative experiments may be described.

Ninety-four grams of phenol were sulphonated with 4 mols. of sulphuric acid (408.1 grams of 96.18 per cent.) to 187.3 per cent. sulphonation. Nitric acid (1.25 mols.; 114.6 grams of 69 per cent.) was added in the cold. After mononitration, 450 c.c. of water were added, then 2.75 mols. of nitric acid, and the mixture was heated at 100° for twelve hours. The yield of picric acid (m. p. 120°) was 80.8 per cent. of the theoretical.

In the other experiment, 94 grams of phenol were sulphonated with 2 mols. of sulphuric acid to 133.2 per cent. sulphonation. After cooling, a further 2 mols. of sulphuric acid were added and then 1.75 mols. of nitric acid. After dilution with 450 c.c. of water, nitrolysis was carried out exactly as described in the previous experiment. The yield of picric acid was 79 per cent. of that theoretically possible; the acid also melted at 120°, but its appearance was inferior.

(d) 4-Nitrophenol-2-sulphonic Acid.

This acid has been obtained by sulphonation of *p*-nitrophenol with fuming sulphuric acid (Post, *Annalen*, 1880, **205**, 38; Körner, *Jahresb.*, 1872, 604), but not with chlorosulphonic acid (Armstrong, *Zeitsch. Chem.*, 1871, 322). Stuckenberg (*Annalen*, 1880, **205**, 45) obtained the same acid by nitration of phenol-*o*-sulphonic acid.

The first of these operations was difficult to carry out (compare Graham and Knecht, *J. pr. Chem.*, 1906, [ii], **73**, 519), the second is to be avoided on account of the difficulty in obtaining the necessary phenol-*o*-sulphonic acid. The following method has been worked out and found satisfactory.

p-Chloronitrobenzene is sulphonated (Claus and Mann, *Annalen*, 1891, **265**, 88; P. Fischer, *Ber.*, 1891, **24**, 3194) and 1-chloro-4-nitrobenzene-2-sulphonic acid isolated. It is unnecessary to follow Claus and Mann in first preparing the barium salt if the following method is adopted:—100 grams of *p*-chloronitrobenzene and 600 grams of fuming sulphuric acid (10–12 per cent. of SO₃) were heated for five hours in an oil-bath at 120–130°, and the cooled product was poured into 1.5 litres of cold water. On removal of a small part of the sulphuric acid by the gradual addition of barium carbonate to the warm solution, a point was soon reached at which crystals of the sulphonic acid began to appear. The mixture was kept until the next day, when the solid mass was filtered off and extracted with hot water. The barium sulphate was removed, and the filtrate deposited 110 grams of chloronitrobenzenesulphonic

acid on cooling, the yield being more than 63 per cent. of the theoretical (Found: N = 5.37, 4.98; S = 12.12; *M* (by titration) = 272.6. $C_6H_4O_5NClS \cdot 2H_2O$ requires N = 5.12; S = 11.72 per cent.; *M* = 273.5).

In order to hydrolyse the chloronitrobenzenesulphonic acid, 15 grams of the free hydrated acid were dissolved in 50 c.c. of water and 6.8 grams of sodium hydroxide (slight excess over 3 mols.) added. After boiling for one and a half hours, and another 25 c.c. of water having been added, a deep yellow, crystalline salt was deposited on cooling. Some of the salt was lost, so that only 9 grams were collected.

The salt proved to be the disodium salt, crystallising with 2 molecules of water, described by Korner (Found: H_2O = 12.16; Na = 15.3. Calc., H_2O = 12.04; Na = 15.4 per cent.). 4-Nitrophenol-2-sulphonio acid was not examined with regard to its nitrolysis.

(e) 2:6-Dinitro-4-sulphonic Acid.

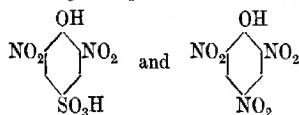
The first attempt to prepare salts of this acid was made by nitrating sodium phenol-4-sulphonate in concentrated sulphuric acid: a mixture of 80 grams of the crushed anhydrous salt with 160 grams of 96 per cent. sulphuric acid was cooled by ice and 58 grams of nitric acid (*d* 1.5) were run in, the temperature being kept low. Towards the end of the reaction, the temperature rose to 60° and the mixture became very pasty. On the next day the solid mass was dissolved in the minimum amount of cold water and the solution poured into a warm solution of 200 grams of crystallised sodium sulphate in 200 c.c. of water. On keeping, a pale yellow salt settled out, which was collected, and dried as completely as possible at 100°. The material was still somewhat damp and in the crude condition weighed 200 grams.

At first the salt was taken to be sodium picrate mixed with picric acid; the latter was probably present to some extent, but, as will be seen below, 2:6-dinitrophenol-4-sulphonic acid gives tests similar to the isopurpuric and picramic acid reactions. Picric acid was not present in any considerable amount, because only a green coloration was produced with ammoniacal copper sulphate, but no crystals were deposited. Further quantities of the required salt were prepared from sodium 2-nitrophenol-4-sulphonate, following the directions given by Beyer and Kegel (D.R.-P. 27271; Friedländer, "Fortschritte der Teerfarbenfabrikation," I, 324) for the preparation of the corresponding potassium salt.

The salt obtained from the strongly acid solution crystallised from a small quantity of boiling water in pale yellow plates,

the yield of purified material being only 37 grams (Found: $H_2O = 15.84$; $Na = 6.52$, 6.95 . $C_6H_3O_3N_2SNa \cdot 3H_2O$ requires $H_2O = 15.88$; $Na = 6.96$ per cent. Found: in the anhydrous salt, $S = 11.96$. Calc., $S = 11.19$ per cent.). It was mentioned above that the salt was at first mistaken for picric acid. The yellow plates much resemble picric acid, but are very readily soluble in water.

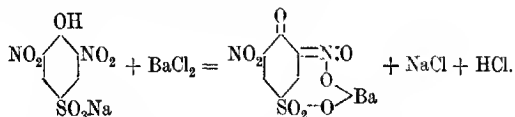
The ammoniacal aqueous solution gives a red colour with a solution of potassium cyanide; this was mistaken for the isopurpuric acid reaction, with which it evidently corresponds. The reaction is interesting as showing the equivalence of the two structures—



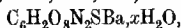
as far as the replacement of the hydrogen atoms in positions 3 and 5 by cyanogen and the reduction of one nitro-group are concerned.

With ammonium sulphide, the red coloration corresponding with the picramic acid reaction is only slowly produced. The distinction from sodium picrate is shown on addition of concentrated sulphuric acid to the saturated aqueous solution, no precipitate being produced. It is interesting to note that Marquoyrol and Carré (*Bull. Soc. chim.*, 1920, [iv], 27, 127) obtained sodium 2:6-dinitrophenol-4-sulphonate by the further nitration of the mononitrophenol-*p*-sulphonate.

The Barium Salt.—This was obtained from the sodium salt by precipitating its solution with barium chloride solution. The precipitate was collected and crystallised from a large quantity of boiling water, in which it is somewhat sparingly soluble. It is nearly insoluble in cold water. The small, orange-red needles contain water of crystallisation and are derived by displacement of two hydrogen atoms in the acid by barium



Balentine (*Annalen*, 1880, 202, 358) described a salt,



as being nearly insoluble in water, and Bertram described a salt, $C_6H_2O_3N_2SBa \cdot 3\frac{1}{2}H_2O$, as belonging to the monoclinic system (*Jahresb.*, 1882, 368). In order to get the salt to constant weight, it was found necessary to heat it at 150° ; the water content does not agree with Bertram's result (Found: $H_2O = 10.55$; $Ba = 30.58$).

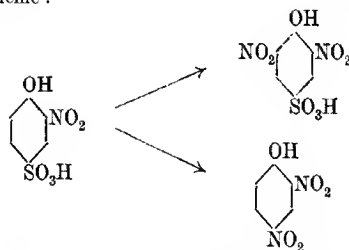
$C_6H_2O_8N_2S \cdot Ba, 2\frac{1}{2}H_2O$ requires $H_2O = 10.13$; $Ba = 30.92$ per cent.). The anhydrous salt is crimson.

The Free Acid.—A solution of the barium salt in hot water was treated with dilute sulphuric acid until no further precipitate was formed, the barium sulphate filtered off, and the solution evaporated. After concentration to a small bulk, small, transparent crystals were deposited, which were yellow when moist, but colourless when dry. After recrystallisation, the melting point of the hydrated acid was about 111° (not sharp); the sulphur content corresponded with 2 molecules of water of crystallisation, not with 3 molecules as described by Brunnemann (*Annalen*, 1880, **202**, 348) (Found: $S = 10.9$; $H_2O = 11.4$. $C_6H_3O_8N_2S, 2H_2O$ requires $S = 10.7$; $H_2O = 12.0$ per cent.).

The free acid gave a red coloration with ammonium sulphide on keeping for some time.

It was previously mentioned that 24 grams of material separated during the boiling of the sodium phenolsulphonate with dilute nitric and sulphuric acids. This was found to melt at $113\text{--}114^\circ$, and there was no depression when it was mixed with 2:4-dinitrophenol. The original, low melting point may be ascribed to admixture of picric acid.

The action of a hot diluted mixture of nitric acid and sulphuric acids on 2-nitrophenol-4-sulphonic acid may be represented by the following scheme :



When no excess of sulphuric acid is present, the second reaction predominates. Since dinitrophenol is converted into picric acid only by nitration in a mixture of concentrated sulphuric and nitric acids, it is evident that a predisposing cause of the formation of low-grade picric acid (due to admixture of dinitrophenol) is to be found in the presence of phenolmonosulphonic acid in the sulphonated mixture, and that this may be largely remedied by nitration in presence of an excess of sulphuric acid.

Continued action of dilute nitric acid on 2:6-dinitrophenol-4-sulphonic acid, can, however, give rise to picric acid. This explains the fact that good results have been obtained in practice when

phenol has been subjected to a low initial sulphonation, but has been subsequently mixed with waste acid, that is, with a considerable excess of sulphuric acid, and subjected to a thorough after-nitration.

Under such conditions, one may expect the formation of 2:6-dinitrophenol-4-sulphonic acid rather than 2:4-dinitrophenol; the former will give picric acid with ease, whilst the latter will not.

The sulpho-group is readily replaced by bromine. A solution of sodium 2:6-dinitrophenol-4-sulphonate was treated with bromine water in slight excess; the yellow, crystalline precipitate, after being washed and dried, melted at 76°. After recrystallisation from hot water, it melted at 77–78°.

The same compound was also obtained from the free acid and bromine water. Korner (*Jahresb.*, 1875, 339) obtained the same compound by bromination of 2:6-dinitrophenol and gave the m.p. as 85.6°. As there seems to be some discrepancy in the literature as to the melting point of 4-bromo-2:6-dinitrophenol, a specimen was prepared by the bromination and subsequent nitration of *o*-nitrophenol (Armstrong and Prevost, *Ber.*, 1874, 7, 922). No lowering of the melting point was observed when a portion of this specimen was mixed with that produced from the dinitrophenolsulphonic acid by the addition of bromine; the orientation of the dinitrophenolsulphonic acid was thus confirmed (Marqueyrol and Carré, *Bull. Soc. chim.*, 1920, 27, 127, give 83° as the melting point of 4-bromo-2:6-dinitrophenol).

An attempt to moderate the violence of the reaction, in the nitration of 4-bromo-2-nitrophenol by a mixture of sulphuric and nitric acids, was made by nitrating in the presence of acetic acid. This, however, led to the production of picric acid (the replacement of bromine by the nitro-group is worth noting).

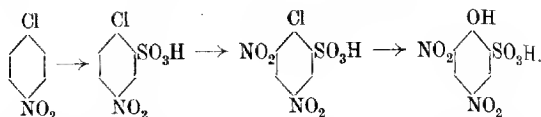
Nitration of 2:6-dinitrophenol-4-sulphonic Acid.

(Heating at 100° for eight hours.)

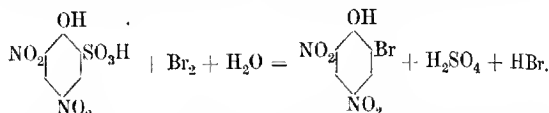
Expt.	Sodium salt (0.1 mol.). Grams.	Sulphuric acid (94 per cent.). Grams.	Water. Grams.	Nitric acid (67 per cent.: 0.21 mol.). Grams.	Yield. Grams.	Yield per cent.	M. p.
1	34	60	0	20	19	82.2	121°
2	"	60	20	"	19	82.8	120
3	"	50	30	"	21.1	91.7	120–121
4	"	40	40	"	20.4	88.8	120
5	"	20	60	"	18.4	80.3	118–119

(f) 4:6-Dinitrophenol-4-sulphonic Acid.

This acid was prepared substantially by Ullman and Herre's method (*Annalen*, 1909, 366, 114). *p*-Chloronitrobenzene was successively sulphonated, nitrated, and hydrolysed;



The orientation of the groups was confirmed by treating the salt in aqueous solution with bromine water. The precipitate melted at 118.5°. 2-Bromo-4 : 6-dinitrophenol melts at 118.2° :



4 : 6-Dinitrophenol-2-sulphonic acid, like its isomeride, may be derived from 6-nitrophenol-2 : 4-disulphonic acid by partial nitrolysis. Marqucyrol and Carré (*Bull. Soc. chim.*, 1920, [iv], 27, 127) have isolated this compound from the mother-liquors obtained in the manufacture of picric acid in larger quantities than the isomeride.

In a particular experiment made by the present author, the former yielded 89 per cent. of the theoretical amount of picric acid after nitrolysis at 100° for only two hours.

(g) 6-Nitrophenol-2 : 4-disulphonic Acid.

Although this acid must be produced from phenol-2 : 4-disulphonic acid by the action of nitric acid, it is strange that it does not seem to have been isolated from the picric acid mixture.

It was first prepared by nitrating (1 mol. of HNO_3 , *d* 1.5) phenol-disulphonic acid liberated from the barium salt in presence of four times its weight of concentrated sulphuric acid, the mixture being externally cooled by ice during the process. The mixture having been diluted with four times its volume of water, barium carbonate was added, the solution boiled, and the barium salt isolated in the usual manner. The yellow salt turns red on heating at 120°, but regains its yellow colour on exposure to air after cooling. On account of the avidity with which water was absorbed, the anhydrous salt was analysed; it contains three equivalents of barium [Found : $\text{Ba} = 39.9$. $(\text{C}_6\text{H}_2\text{O}_6\text{NS}_2)_2\text{Ba}_3$ requires $\text{Ba} = 41.0$ per cent.].

For the preparation of considerable quantities of the barium salt, intermediate isolation of the phenoldisulphonic acid is unnecessary.

Phenol (500 grams) and 2000 grams of oleum (23 per cent.) were heated at 100° for four hours, then cooled, diluted by the addition of small pieces of ice (about 150 grams), and nitrated by the slow addition of 254 c.c. of nitric acid (*d* 1.5). The mixture was cooled

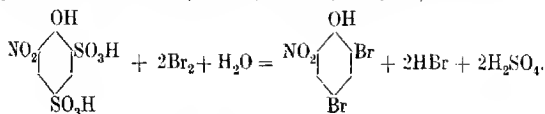
externally and the temperature was not allowed to exceed 20°. The mixture, which formed a solid mass on keeping, was dissolved in 8 litres of water, neutralised with barium carbonate (about 3½ kilos.), and worked up in the manner previously described. The crude barium salt was recrystallised twice, the weight obtained being 850 grams. The salt was dehydrated before analysis (Found : Ba = 40·7 per cent.).

The Free Acid.—This may be obtained from the barium salt, but an alternative process has been worked out.

Phenoldisulphonic acid prepared from its barium salt was nitrated in the manner previously described; on keeping for some days, the nitrophenoldisulphonic acid crystallised out. It was filtered over asbestos and the adherent sulphuric acid removed by the following procedure: the solid was washed repeatedly with small quantities of ether, then dissolved in the minimum quantity of ether and a considerable excess of chloroform added. The acid was filtered off and the process repeated. As the sulphuric acid is removed, the solubility in ether diminishes.

After a third precipitation by chloroform, the acid was dissolved in water, the solution filtered, and evaporated at 100°. After some hours, crystals began to form, and concentration was then continued in a vacuum desiccator. The acid was drained on tile, and obtained as colourless, silky needles. 6-Nitrophenol-2:4-disulphonic acid is extremely deliquescent; the aqueous solution is pale yellow, and becomes intensely yellow on addition of alkali (Found: N = 3·88. $C_6H_5O_6NS_2 \cdot 2H_2O$ requires N = 4·18 per cent. The equivalent weight, by titration, = 113·0. Calc., 111·7). Since the titration is not very easily performed, it is possible that the acid crystallises with $3H_2O$ (Calc., N = 3·96 per cent.).

Bromine water added to a solution of the free acid gave a precipitate which melted at 117° after washing and drying, and at 117·5° after recrystallisation from water. 2:4-Dibromo-6-nitrophenol melts at 117·5° (Arzruni, *Jahresb.*, 1877, 548):



Formation of 2:4-Dinitrophenol.

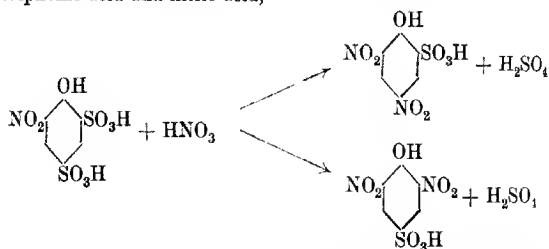
It has been pointed out that dinitrophenol is formed by nitrolysis of 2-nitrophenol-4-sulphonic acid. The latter compound probably owes its origin as a general rule to phenol-4-sulphonic acid (low degree of sulphonation).

Nitrolysis of Sulpho-groups in the ortho- and para-Positions.

It was stated in the introduction that a sulpho-group is more readily displaced by the nitro-group from position 4 than from position 2. This is shown by the following experiment. It was thought advisable to avoid complications due to replacement of hydrogen in the nucleus, and therefore 6-nitrophenol-2:4-di-sulphonic acid was selected for the experiment.

The trisodium salt (77.5 grams; 0.2 mol.), containing 5.86 per cent. of moisture, was finely crushed, mixed with 68.6 grams of sulphuric acid (96 per cent.), the mixture was diluted with its own volume of water, and heated for two hours at 100° with 22.84 grams of nitric acid (69 per cent.; 1.25 mols.). The reaction was not violent, brown fumes were evolved, and, on cooling, the whole mass solidified; 54 grams of material were isolated. The major portion was separated into three fractions. The first (7 grams) consisted essentially of picric acid, the second (2.5 grams) also contained picric acid and was neglected. The main crop (32 grams) was fractionally crystallised; the four crops obtained, when treated with bromine, gave brown compounds with melting points varying from 113° to 118°. No depression of melting point was observed on admixture with a specimen of 2-bromo-4:6-dinitrophenol (m. p. 118.2°); the bromo-compound must then have been produced from 4:6-dinitrophenol-2-sulphonic acid. Care must be taken that bromine is not added in large excess to the dinitrophenolsulphonate; Marquoyrol and Carré (*loc. cit.*) have shown that under this condition 4:6-dinitrophenol-2-sulphonic acid gives rise to 4-bromo-2:6-dinitrophenol to a large extent.

Thus of the two initial reactions between 6-nitrophenol-2:4-disulphonic acid and nitric acid,



the first must be preferred, even if it does not take place exclusively. Confirmatory evidence was afforded by heating 2:6-dinitrophenol-4-sulphonic acid and 4:6-dinitrophenol-2-sulphonic acid under similar conditions with a mixture of water and nitric and sulphuric

acids. Reaction began immediately with the first of these acids, but was not evident with the second acid during the first half-hour. After being heated for two hours, the first mixture gave a yield of 91.7 per cent. of picric acid, and the second a yield of 81.6 per cent.

Formation of Oxalic Acid.

The quantity of oxalic acid produced during the nitration of :

A. Sodium phenol-4-sulphonate, $C_6H_5O_4SNa \cdot 2H_2O$,

B. Sodium 2-nitrophenol-4-sulphonate, $C_6H_4O_6NSNa \cdot 3H_2O$,

and

C. Sodium 2 : 6-dinitrophenol-4-sulphonate, $C_6H_3O_8N_2SNa \cdot 3H_2O$,

was determined under varying conditions. The formulae indicate the form in which the material was weighed. The salt was dissolved in water, the solution made up to a definite volume, and an aliquot portion was rendered alkaline with ammonia and precipitated with calcium chloride. The precipitate of calcium sulphate and oxalate was washed free of picric acid, and the oxalic acid estimated by permanganate.

	Weight in grams of reagents employed in the nitration of 1 gram-mol. of the salt.			Grams of oxalic acid produced from 1 gram-mol. of the salt.
	94% H_2SO_4 .	Water.	67% HNO_3 .	
A	596	0	399	12.35
A	366	400	405	14.21
B	612	0	300	4.67
B	605	200	304	3.77
B	507	300	306	10.49
B	448	400	295	10.41
B	200	600	300	14.15
C	600	0	200	2.18
C	600	200	200	0.45
C	391	391	200	0.91
C	200	600	200	0.34

The table shows that the introduction of the nitro-group into the phenolsulphonate before dilution and further nitration to picric acid increases the stability.

The foregoing work was carried out at H.M. Chiswick Laboratory, Department of Explosives Supply, in 1917—1918, and is now published with permission of the Director of Staff Duties.

The author wishes to thank Dr. J. T. Hewitt, F.R.S., formerly Director of the Chiswick Laboratory, for his advice given throughout the course of this work.

UNIVERSITY COLLEGE,
EXETER.

[Received, November 17th, 1921.]

OBITUARY NOTICES.

ALBERT ERNEST BELLARS.

BORN AUGUST 25TH, 1880; DIED APRIL 23RD, 1921.

ALBERT ERNEST BELLARS was the son of the late Alderman E. B. Bellars of Wisbech. He was educated at Wisbech Grammar School under Mr. A. W. Poyser and at Magdalene College, Cambridge, where he held a Holmes Exhibition. After taking his degree in the Natural Sciences Tripos in 1902, he was appointed Assistant Demonstrator in the laboratory of Gonville and Caius College under Mr. M. Pattison Muir. Later he undertook the supervision in chemistry of students in Gonville and Caius and in Magdalene Colleges. Between 1903 and 1910 he was engaged in research work, the results of which have appeared in the *Transactions of the Chemical Society* and in the *Proceedings of the Cambridge Philosophical Society*. At Cambridge he was an enthusiastic teacher and very popular with students in the laboratory and in the college classes under his supervision. As a colleague in research, he was a skilful and accurate experimenter, and he never tired in his determination to solve a problem. No failure disheartened him, and his cheery optimism gave stimulus to work in which he was engaged. With the writer he published between 1903 and 1907 the results of four investigations which have appeared in the *Transactions*. In 1911, after the closing of the chemical laboratory of Gonville and Caius College, he was appointed Professor of Chemistry at the Rangoon University College on the recommendation of Sir W. J. Pope, and soon proved himself to be a stimulating lecturer and teacher. Last year he was appointed the first Professor of Chemistry in the new University of Rangoon.

The splendidly-equipped chemical laboratory at University College is a monument to his thoroughness and foresight, and a long list of those who have graduated in science in Burma during the last ten years bears testimony to his unwearying labour and to the activity of the interest in that branch of science of which he himself was so keen a student. The claims of teaching work left little opportunity for research until lately, when in the new laboratory he was able to resume it. Serious throat trouble compelled him to come to England this year for an operation, which was at first successful, but a sudden attack of hæmorrhage occurred later, which was fatal. In December, 1919, Professor Bellars married Miss Beryl Coxon, only daughter of Major Coxon, of King's Lynn.

Norfolk. She returned to England with her husband this year and was with him at his death. Professor Bellars leaves a posthumous son born a week after his death. In Burma, great sympathy is felt for his widow, who had been in the colony only a little more than a year when her husband was invalided home. Bellars was a keen sportsman in every sense of the word. At Cambridge he was captain of his college cricket team and played regularly in the Cambridge County Eleven. He was an enthusiastic skater of the fen style and a golfer. In the Long Vacations he was one of the band of climbers of the Alpine Club and was associated with the late Dr. H. O. Jones in several of his ascents. In the Easter Vacations he climbed in Snowdonia or in the Lake District. While in Rangoon he took a keen interest in all matters connected with sport and volunteering at the University College and officiated regularly at the local athletic meetings.

His sudden and early death is much to be deplored. Bellars was the ideal type of colonial University Professor. The soundness of the knowledge of his subject combined with a driving power and personality commanded the loyalty and respect of his students, not only in the lecture room, but also in the college sports. He was of the true type of teacher and leader of men, such as have built up the British Empire, and yet he was of a retiring disposition and never sought popularity outside the circle in which his main interests lay. He was devoted to his work and to his home.

R. S. MORRELL.

EDWARD JOHN BEVAN.

BORN DECEMBER 11TH, 1856; DIED OCTOBER 17TH, 1921.

EDWARD JOHN BEVAN, son of Edward Bevan, of Birkenhead, was born in 1856. After a private school education he received a training in chemical science which may be described as irregular.

Beginning at the age of seventeen with the routine of laboratory control of alkali processes in the service of the Runcorn Soap and Alkali Co., he made friendships with certain pioneer workers in that industry, who usefully influenced his career by advising systematic training at the Owens College—then a leading centre of research. The meeting with C. F. Cross resulted in a student friendship which developed into one of collaboration, both leaving the College (1879) to undertake research work in the cellulose industry, Bevan's sphere being that of paper-making. Problems of common interest were investigated, of which results were pub-

lished in the *Journal of the Chemical Society* (1882). It was already evident that the field of work entered on, promised results in proportion to industry; it was decided to make a definite adventure, and "Cross and Bevan," migrating to London, were able to find a provisional working home in the Jodrell Laboratory, Kew, through the friendly offices of H. E. Armstrong, Hugo Müller, and Thiselton-Dyer.

The scope of research widened to include the physiology of the vegetable fibres, the equilibrium of the fibre substances as chemical individuals in relation to water-oxygen conditions, hence a special study of cellulose reactions with hydrolytic agents and oxidants; and in development of the natural history aspect of the subject, the working out of a comprehensive scheme of analysis of the fibres and fibre-aggregates, the raw materials of the textile and paper-making industries.

The scientific data thus accumulated were then applied in developing industrial inventions, such as the bisulphite process of treating wood for the preparation of cellulose ("pulp"), then in its infancy, and pioneered in this country by C. D. Ekman: and textile bleaching processes, for example, those of Thompson, Hermite (electrolytic), and W. Mather. The Colonial and Indian Exhibition provided a sphere of active work in vegetable fibres, and established the method of analysis and evaluation of these raw materials as a "standard," subsequently to be generally accepted as such. Concurrently with these technical activities, the systematic research work on cellulose and its derivatives was followed up and investigations of alkali-cellulose (mercerisation) and benzoates (Baumann's method) led in logical sequence to the discovery of the xanthogenic hydrate-ester series of derivatives, patented in the joint names, and the basis of the now well-known "viscose" industries.

The formal partnership "Cross and Bevan," and its establishment at New Court, Lincoln's Inn (1885), led to outside activities, such as those connected with patent litigation, in which Bevan showed his exceptional abilities, and decided leanings to the professional side of chemical science. Applying for the post of Public Analyst under the Middlesex County Council, he was appointed (1892), and held the office to the date of his death. As necessary incidents of this position, he became progressively influential in the Society of Public Analysts, of which he was sometime President, and on the Council of the Institute, devoting himself with his usual thoroughness to its interests and high aims.

Bevan's career expresses his whole-hearted devotion to Science, for his varied activities were all marked and hall-marked by the

severe discipline of the pursuit of "the Truth" as "the whole Truth and nothing but the Truth," as we chemists know the truth of an experimental science, with the uncompromising laws under which we work for its establishment.

With these qualities were associated those which express themselves in good fellowship. Bevan was popular, as he was genial and generous. His surviving relatives treasure the many expressions of affection and regard contained in letters from his brother chemists.

For a complete and chronological record of the publications in which Bevan was associated with the writer, those who may be interested are referred to the *Paper Trade Review* of January 28th, 1921.

C. F. Cross.

EDWARD KINCH.

BORN AUGUST 19TH, 1848; DIED AUGUST 6TH, 1920.

EDWARD KINCH was born at Henley-on-Thames, and was educated at the Grammar School there. His father, Charles Kinch, was a pharmaceutical chemist, and would seem to have been a very energetic man, for he also had a printing and stationery business, published a local paper, and took an active part in the management of the affairs of the town.

Although Edward Kinch spent his early life there, it is not in association with Henley that one thinks of him, but with that agricultural district on the Upper Thames where the counties Berkshire, Wiltshire, Oxfordshire, and Gloucestershire meet. There on the Berkshire bank of the Thames lies the scattered village of Eaton Hastings, and at the "Grange," a charmingly old-fashioned, somewhat rambling farmhouse, many generations of the Kinch family had dwelt and farmed their own land, whilst relations of theirs were to be found in many of the large farms in the district lying between Farringdon and the Cotswolds. Amongst them were men who have made their mark in agriculture, such as Charles Hobbs of Maisey Hampton and his son Robert Hobbs of Kelmscott, both so well known as successful breeders of sheep. It may be mentioned incidentally that the picturesque Manor House at Kelmscott, standing opposite to Eaton Hastings on the Oxford bank of the Thames, which figures so much in the art annals of the Victorian era as the home of William Morris, and for a time also of D. G. Rossetti, belonged to a widowed aunt of Edward Kinch who lived with her brother William at the Grange. It was in his frequent

visits to these relations probably that Edward Kinch acquired that interest in agriculture that became the dominant feature in his life.

On leaving school, Kinch went to the Royal College of Chemistry in Oxford Street, where he studied for some years under Prof. (later Sir Edward) Frankland. His first appointment (1869) was that of chief assistant to Prof. (later Sir Arthur) Church at the Royal Agricultural College, Cirencester, and thus began the connexion with the institution with which later he was so intimately associated. He held this post until the latter part of 1872; he then joined the staff of the Royal College of Chemistry, which, with some sections of the Royal School of Mines, had just been transferred to the new buildings in the Exhibition Road, South Kensington, to form the nucleus of that institution which after many changes of name is now known as the Imperial College of Science and Technology. After some years spent in teaching in these laboratories, Kinch for about a year held the position of Superintendent of Minerals at the India Museum, South Kensington. In 1876 he accepted the post of Professor of Chemistry at the Imperial College of Agriculture, Komaba, Tokyō, Japan, in the organisation of which he took an active part. At this time Japan was still in large part closed to Europeans, but in the college vacations Kinch was allowed to travel freely about the country, and had opportunities such as fell to few others of seeing "Old Japan." One considerable drawback, however, was that in many of the out-of-the-way districts it was impossible to supplement in any way the meagre vegetable diet of the natives—the result to a European being semi-starvation.

In 1881, Kinch returned to England on his appointment as Professor of Chemistry at the Royal College of Agriculture, Cirencester, a post which he held until the closing down of the College in 1915 on account of the war.

Prof. Kinch married, in 1889, Edith, daughter of the Rev. George Huntingdon, vicar of Tenby, but their happy married life was terminated by her death a year later.

On the closing of the Cirencester College, Kinch retired from active life and went to live at Haslemere, where he occupied himself with his garden, and with Japanese art, a subject in which he was greatly interested. His residence in Japan had enabled him to form a small but admirable collection of curiosities and art work. A serious illness in 1918 left him with very impaired health, and he died on August 6th, 1920.

Edward Kinch was a man who devoted himself heart and soul to his students and to the interests of the Royal Agricultural College, Cirencester, where he spent thirty-four years of his life. Singularly unassuming, and of very retiring nature, he was beloved by those

who came under his influence, and the fruits of his sound and careful training of his students were manifested by many of them in subsequent spheres. It was for his college and his students that he lived, and it was in this connexion, rather than in public life, or in written contributions to science, that he excelled. His principal literary contribution was the revision and practical re-writing, in 1906, of the well-known book for agricultural students, "Church's Laboratory Guide," of which a ninth edition appeared in 1912. (Occasional papers from him have also appeared in the *Journals* of the Chemical Society, the Royal Agricultural Society, and the Surveyors' Institute, but most of his contributions were given in the *Agricultural Students' Gazette*, issued from the Cirencester College. Kinch was a sound, rather than a progressive, chemist, and a teacher, rather than an investigator, but he was a man held in much esteem by those who knew him. In conclusion, the words of a former student, Lord Bledisloe, intimately acquainted with the affairs of the College, may be quoted: "If and when the worthy history of England's premier agricultural college comes to be written, no name will rank higher in its annals than that of Edward Kinch, and no one will be deemed to have wrought a more beneficial influence in promoting the high reputation of the College and the progress of Agricultural Science in the British Empire."

Prof. Kinch served on the Council of the Chemical Society, 1887-1892; at an earlier period, 1872-1875, he was on the Journal staff as an abstractor in Agricultural Chemistry. A. J. G.

HENRY RONDEL LE SUEUR.

BORN JANUARY 1ST, 1872; DIED JULY 9TH, 1921.

H. R. LE SUEUR was born at Trinity, Jersey, on January 1st, 1872, the son of F. C. Le Sueur. He was at a private school until 1887, after which he spent two years in the laboratory of a Jersey analyst, Mr. F. W. Toms, and then entered University College, London, taking the Honours Chemistry course. He graduated B.Sc. of London University in 1893 and obtained the D.Sc. degree in 1901. He was a Fellow of the Institute of Chemistry (Associate 1898) and a member of its Council from 1914 to 1917: a Fellow of this Society (1895), a member of Council (1907-1911), and at the time of his death was one of its Secretaries.

After graduating in 1893, Le Sueur spent one year in carrying out research work on the properties of dehydracetic acid (Collie

and Le Sueur, T., 1894, 65, 254), and in the following year took up a junior teaching post in the Medical School of St. Thomas's Hospital. Possessing the faculty of imparting knowledge to others, Le Sueur rapidly developed into a teacher of the very first order, and it is a remarkable fact that one possessing such pronounced capabilities in this direction should have remained attached to this one Institution for the twenty-seven years of his career. The writer is well acquainted with the happy atmosphere of St. Thomas's, and no doubt this weighed with Le Sueur, especially as from 1904 he occupied the senior teaching post, but it is none the less strange that his exceptional teaching capacity was not more generally recognised.

There was only one break in the twenty-seven years during which Le Sueur was connected with St. Thomas's, namely, that caused by the War. He was gazetted major, Royal Engineers, in 1915 and with Major J. T. Hewitt was ordered to Gallipoli to watch and advise on possible developments in gas warfare. There can be little doubt that the illness which he contracted there seriously undermined his health, for he was never in reality the same high-spirited man again. On his return to England, after being in hospital in Egypt, he became one of the chief experimental officers at the R.E. Experimental Station, Porton, where he was attached until the end of 1917. He was then ordered to the United States to assist in the preparation of the American Gas Warfare Experimental Station, and he remained there until after the signing of the Armistice.

As a research worker, Le Sueur was not prolific, his total published papers amounting to twenty-four; this is largely accounted for by the fact that research was regarded by him as a pleasurable relaxation from his teaching duties, which always came first. He thoroughly enjoyed every minute he was able to devote to experimental work, but when accumulated results made the writing of a paper desirable he was very obviously bored. His researches concerned mainly the fatty acids and their hydroxylated derivatives, and may be divided into three groups. In one, he studied the action of heat on the α -hydroxycarboxylic acids and showed that it is possible to descend the series of fatty acids, step by step, according to the scheme, $R \cdot CH_2 \cdot CO_2H \rightarrow R \cdot CHBr \cdot CO_2H \rightarrow R \cdot CH(OH) \cdot CO_2H \rightarrow R \cdot CHO \rightarrow R \cdot CO_2H$. A somewhat similar process led, in a second series of experiments, to a simple method for the preparation of secondary amines, thus: $R \cdot CHBr \cdot CO_2H \rightarrow R \cdot CH(NHAr) \cdot CO_2H \rightarrow R \cdot CH_2 \cdot NHAr + CO_2$, whilst the third group of researches, on the action of fused potassium hydroxide on the dihydroxy-acids obtained by oxidation in the oleic acid series,

revealed an unusual transformation, namely, the movement of a heavy radicle within the molecule of an aliphatic compound. The change is represented thus: $R \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_n \cdot CO_2H \longrightarrow OH \cdot CH_2 \cdot CR(OH) \cdot [CH_2]_n \cdot CO_2H \longrightarrow CO_2H \cdot CR(OH) \cdot [CH_2]_n \cdot CO_2H$. The elucidation of the constitution of the hydroxydicarboxylic acids formed in this way led, incidentally, to the discovery of heneicosoic acid, a missing member of the simple fatty acid series.

In manner Le Sueur was quiet and reserved, not to say shy; few knew him well, for his efforts to disguise the above characteristics sometimes gave quite a wrong impression of the real man. His great outstanding quality was loyalty, which governed his every action and was one of the main causes of the loving regard in which he was held by his intimate friends. As a Jerseyman, Le Sueur had an intense feeling of local patriotism, and his friends knew well his loyalty to the "Duke of Normandy." He was one of the founders of the Jersey Society in London and one of its most active members during more than twenty years, being chairman of its council at his death. He spoke a dialect of the ancient Norman-French language fluently and with historical pride, and it was because of his love for his native land that he desired to be laid to rest in Jersey.

A. W. CROSSLEY.

GEORGE BLUNDELL LONGSTAFF, M.A., M.D. (OXON.),
F.R.C.P., F.S.A., F.L.S., F.C.S., F.G.S., J.P.

BORN FEBRUARY 12TH, 1849; DIED MAY 7TH, 1921.

In the late George Blundell Longstaff the scientific, the artistic, and the practical temperaments were so nicely blended that it would be impossible to say which of these qualities preponderated in his attractive and versatile nature. Those who made his acquaintance as a field naturalist and had occasion to note his keen powers of observation, his untiring activity as a collector, and his readiness to appreciate the scientific bearing of the facts that he and others accumulated, might not unnaturally be surprised to find that his technical knowledge of the building craft was the admiration of experts, and that his judgment on all matters of the graphic and plastic arts was highly valued by the most experienced critics.

It is interesting to call to mind that many of the most conspicuous traits in Longstaff's character may be traced back to his ancestry. Thus his father, in early days an associate of "Osmotic Graham," was noted for his devotion to chemistry; to the Dixon

strain may be attributed his interest in everything practical and constructive; while the extraordinary energy with which he worked at entomology may be considered not improbably to be foreshadowed in the stock from which sprang Spence of "Kirby and Spence."

Born at Wandsworth in 1849, Longstaff was the second son of Dr. George Dixon Longstaff, and of Maria, daughter of H. Blundell, of Hull. At Rugby he came under the influence of Archbishop Temple, then Headmaster, and of Archdeacon J. M. Wilson, then Master in Natural Science and Mathematics. Each of these great teachers left a strong impress on the mind and character of their pupil. Proceeding in due course to Oxford, he gained a scholarship in Natural Science at New College, following this up with a First Class in Natural Science. It was while an undergraduate at Oxford that by a deplorable accident he lost the sight of an eye. Throughout his life the condition of his sight was such as to necessitate the greatest care in the use of his remaining eye; and he was compelled to forego many schemes of scientific research which his inclinations would have led him to adopt. But he faced his misfortune with admirable courage, and engaged with vigour and energy in all the pursuits of a kindred nature which still remained open to him. After taking his degree in Arts, he entered at St. Thomas's Hospital, and having passed through his career as a medical student with distinction, he graduated as M.B., subsequently as M.D., at Oxford; and obtained the Membership, eventually the Fellowship, of the Royal College of Physicians. In 1875 he married a daughter of Edward Dixon, of Southampton, a member of a family already connected with his own. The intellectual endowments, the philanthropic ideals, and fine taste of this lady were most congenial to him, and it would have been difficult to find a better-assorted couple. On settling down with his wife and young family, first at Wandsworth and afterwards on Putney Heath, he devoted himself to the study of preventive medicine and vital statistics, paying special attention to all such matters as might benefit the conditions of life among the poorer and less fortunate members of the community. The present writer became associated with him in some of this early work, especially in the investigation of the properties of a much-advertised germicide, and in the statistical aspects of various diseases. This led to a long collaboration in the Registrar-General's Department at Somerset House, many results of which saw the light in his published volume of "Studies in Statistics." Whilst still engaged in work of this kind, he acquired the beautiful estate at Mortehoe, in North Devon, where much of his subsequent life was passed, and where he threw himself with characteristic energy

into the study of the history, antiquities, natural productions, and social conditions of that part of the county. To these rural pursuits he added much varied activity in London, serving on the London County Council as member for Wandsworth from 1889 to 1903; and, as Chairman of the Building Act Committee of that body, taking a principal part in the drafting and passing through Parliament of the London Building Act, 1894. As J.P. both for London and Devon, he gave much time to magisterial duties, and as Guardian of the Poor he found scope for the exercise of his interest in the social conditions of the more indigent classes.

It had always been his desire to travel; and he soon found opportunity to acquaint himself with many remote parts of the earth. At different times he visited Madeira, the Canary Islands, Algeria, Egypt and the Soudan, South Africa, India, Ceylon, China, Japan, North and South America, the West Indies, Australia, and New Zealand. In all of these places he made large collections, principally of insects, and recorded numerous observations of high interest in the elucidation of bionomic questions. The results of these labours in the field of natural history were published by him in several important memoirs, collected some nine years ago in a volume entitled "Butterfly Hunting in Many Lands." The insect collections, which are of great value both in themselves and for the exact data by which each specimen is accompanied, were presented by him to the Hope Department in the University of Oxford. This Department found in him a generous and far-sighted benefactor; it being indebted to him, amongst other donations, for an endowment of £2400 for the provision of an additional assistant. Beside all his other avocations, he found time to take an active part in the work of the Charity Organisation, the Royal Statistical and the Entomological Societies, being at various times Vice-President of the latter two. He was also a Fellow of the Linnean and Geological Societies, of the Society of Arts, and of the Chemical Society. In the last-named he took a special interest, and in the year 1916, to mark the seventy-fifth anniversary of the Society, he made over to it the sum of £1000 for its Research Fund; thus following the example of his father, who in 1876 had given £1000 to establish this Fund. A "Longstaff Medal" is awarded by the Council of the Society every three years for the best series of original investigations in chemistry published in England. Longstaff's munificence was not confined to scientific objects; for many schemes of social improvement were helped by him with ample donations, and he was a liberal benefactor to the Church. He was especially concerned in the planning and building of the new church at Woolacombe, North Devon; and the ancient church

of Mortehoe bears many marks of his generosity; in particular, a beautiful stained-glass window by his friend Selwyn Image, lately Slade Professor of Fine Art at Oxford.

Three years after the death of his first wife he married Miss Donald, a daughter of the late M. H. Donald of Stanwix and Blaithwaite, Co. Cumberland, a lady distinguished for her attainments in conchological science, and with many interests similar to those of her husband.

A man of such varied capacities and of so generous and sympathetic a nature as George Blundell Longstaff was sure to have numbers of attached friends, by whom his death is felt as a grievous personal loss. His memory will be widely cherished as that of an inspiring and stimulating companion, and one of the most considerate and open-handed benefactors of his generation.

F. A. D.

EDMUND JAMES MILLS.

BORN DECEMBER 8TH, 1840; DIED APRIL 21ST, 1921.

PROF. E. J. MILLS, who died on April 21st, 1921, was born in London on December 8th, 1840. He was educated first at the Grammar School, Cheltenham, and then at the Royal School of Mines, where he took the courses of instruction for a degree in science at London University, at that time the only university in Britain granting such degrees. He graduated B.Sc. in 1863, and obtained the doctorate in 1865. There were few candidates for science degrees at that time, and on looking at the list of graduates it is interesting to note that Mills's name appears about equidistant in time between those of Prof. Alex. Crum Brown, in 1862, and Sir William Tilden, in 1871.

In 1861, Mills became assistant to Dr. John Stenhouse, and a year later he was appointed one of the demonstrators in chemistry at Glasgow University, in which capacity he conducted tutorial classes for medical students, a work not very congenial to him, and one for which, from his temperament, he was not particularly well fitted; he was, however, a good laboratory teacher for advanced students. He resigned this appointment in 1865. In 1875 Mills became superintendent of the "Young Laboratory," in Anderson's College, Glasgow, and during his term of office, about the year 1886, that foundation together with Anderson's College, became incorporated in the Glasgow and West of Scotland Technical College, the Young Laboratory appointment being converted into

the Young Chair of Technical Chemistry. His predecessors in charge of the Young Laboratory were W. H. Perkin, sen., 1870-71, and G. Bischof, 1871-75.

Mills was the author of many papers covering a wide field of work. Although his first recorded paper in the *Proceedings of the Royal Society* (1860) is upon bromo- and chloro-phenylamine, his early work inclined more to general and inorganic chemistry, dealing with subjects such as isomerism, statical and dynamical ideas on chemistry, chemical equivalents, etc., and this tendency is seen also in his later papers in the *Philosophical Magazine*, published during 1883, 1884, and 1887. In the *Journal of the Chemical Society* his more important papers are:—"On Aniline Derivatives and Nitrotoluene" (1875-76); "On Potable Waters" (1878-81); "On Chemical Repulsion" (1880-81); "Melting-points" (1882). From 1879 to 1882 he published "Researches on Chemical Equivalence"; from 1878 to 1880 papers on "The Action of Oxides on Salts"; and later, "Researches on Dyeing" in conjunction with Louis Campbell. To the Society of Chemical Industry he contributed papers on the "Quantitative Estimation of Oils and Fats" (1883), "Viscosity Determinations" (1886), and "Oxidation of Aniline" (1894). In his books, Mills did not confine himself to purely scientific matters; for, in addition to two works, "Fuel and its Applications" (published conjointly with E. J. Rowan in 1889) and "Destructive Distillation" (1892), he wrote a volume of poems, "My Only Child" (1895), and "The Secret of Petrarch" (1904).

Mills was elected a Fellow of the Royal Society in 1874, and was an honorary LL.D. of Glasgow University; he was an original member of the Society of Chemical Industry and served on the committee of the Glasgow Section, including two periods as vice-chairman, from 1884 to 1894; and was a member of the Council of the Chemical Society at various times from 1868 to 1906, serving as vice-president from 1912 to 1915.

Mills returned to London, finally settling at West Acton. He spent much of his leisure time in the practice of photography, in which he was a skilled manipulator. He attended many of the meetings of the Scientific Societies to which he belonged, and rendered valuable service to the Chemical Society as a member of the Library Committee, in which he took special interest.

J. M. T.

RICHARD HENRY VERNON.

BORN JANUARY 27TH, 1885; DIED APRIL 9TH, 1921.

RICHARD HENRY VERNON was the elder son of the late Hon. William Vernon, son of the sixth Baron Vernon, and of Mrs. Vernon, daughter of the late General Daniel Marsh Frost, of St. Louis City, U.S.A.

Born in London at 12 Clarges Street, Vernon had a serious illness at the age of nine which left consequences that made it doubtful whether he would be able to stand the English climate. He was therefore educated in Switzerland. He entered the École Cantonale at Lausanne in 1898 and proceeded to the Gymnase Scientifique, which he left with the Certificat de Maturité in 1902. Here he showed powers of work and a capacity for scientific and mathematical subjects which won the highest opinion from his teachers.

It had always been his father's desire that he should receive an American University education, and at the age of nineteen he entered at Cornell. He was then full of high spirits and love of adventure, and it was there that he won a bet that he would walk sixty miles in twenty-four hours. He covered the distance with two hours to spare, although it was in winter and the walk had to be made in the snow. However, he found the environment at Cornell uncongenial. The free open-air life of the Western States had an irresistible attraction for him, and to the concern of his parents he broke off his University career and went to California, where a maternal uncle had an estate. Here he learnt all the craft of the ranch—afterwards at Cambridge he would sometimes amuse his friends by illustrating with a rope some of the skill that he had acquired with the lariat—and for some time he lived an independent life, maintaining himself as "broncho-buster" and cowboy. Drifting in this way from California to Texas, he came at length to the little township of Throsmorton. Here there was a schoolmaster who had some knowledge of physics and with him Vernon became very friendly. The two used to discuss scientific problems together, and Vernon was made by him to realise that he had gifts which were being wasted in the life he was then leading, and was persuaded to return to Europe to continue his education. His parents were at Wiesbaden, and he joined them there and spent six months working in the laboratory of Professor Fresenius. Fresenius recognised his ability and encouraged him to take up chemistry as a profession. Accordingly, in 1907, at the age of twenty-one, he entered the Eidgenössische Technische Hochschule at Zurich, where, after working through the customary four years' course in chemistry, physics, and mathematics, he obtained the

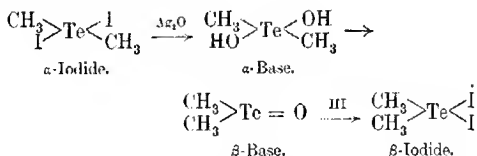
diploma in 1911. He then began, under the direction of Prof. F. P. Treadwell, the work on the electric conductivity of very pure water which was to form the subject of his thesis for the doctor's degree. The greater part of this thesis is occupied with the calculation of the relations between the inductances and capacities of the arms of the Wheatstone bridge which give the sharpest minimum of sound in the telephone. He demonstrated the practical utility of arrangements based on his results, and employed them to examine the methods of obtaining pure water by distillation. After receiving his doctor's degree in the spring of 1914, he began a magneto-chemical investigation of platinum compounds with Prof. Pierre Weiss, but this was cut short by the events of the following August. He was then fishing in the Black Forest and barely succeeded in crossing the frontier at the declaration of war. He hastened to England to offer his services, but was rejected several times on account of eyesight. Ultimately he enlisted in the R.A.M.C., but after serving for a short time with that corps he was transferred to the Royal Engineers, where he became a despatch rider. In 1915 he was granted a commission in the 3rd Battn. of the Dorset Regiment, and in the spring of 1916 proceeded to the Western Front, where he saw much active service, chiefly in the Armentières district and on the Somme. After two long periods of illness in hospital he was pronounced unfit for active service and was transferred for duty to the Chemical Warfare Committee, for whom he worked, first at the Imperial College of Science in conjunction with Prof. Baker on dichlorodiethyl sulphide, and afterwards at Cambridge in the University Chemical Laboratory, where, at the suggestion of Sir William Pope, he began an investigation of the alkyl tellurium compounds.

In July, 1918, Vernon was sent as Chemical Adviser to the Shell Filling Factory at Chittening. Here he rendered services of the greatest value in contriving precautions to be taken in the handling of "mustard gas," in working out methods for cleaning up spills and rendering the waste innocuous, and in training the operatives in the use of the measures which had been devised. It fell to him to grapple with the mischances that not infrequently occurred. When, for example, as happened in the early days of the factory, a defective cock led to a spill of several gallons, it was the Chemical Adviser who had to deal with the emergency. He won the regard and confidence both of the staff and of the operatives; the men of his special anti-gas detachment in particular gave him willing and loyal support. Life in the factory at first was rendered intolerable by the vapour of the "mustard gas," which permeated everything; sometimes, in fact, before the later improvements were introduced.

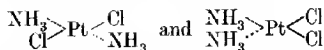
the whole of the workers in a shed would be left on the sick list at the end of a four hours' shift. It was largely through the devotion, and indeed the heroism, of the Chemical Adviser that in spite of everything the factory was able to send out in a steadily increasing stream the shells so urgently needed to enable the troops in the field to reply to the deadly weapon which the enemy had adopted.

By the continuous strain of work such as this Vernon's health was severely tried and at the time of the Armistice he was in hospital very dangerously ill with pneumonia. After a period of convalescence in the south of France he was able to return to Cambridge, and in the spring of 1919 he entered Gonville and Caius College as a research student and resumed his work on the tellurium compounds.

Before going to Chittening Vernon had prepared a number of dimethyltelluronium derivatives. He now examined more closely the base formed by treating dimethyltelluronium iodide in aqueous solution with silver oxide, and thus made the highly interesting discovery that when the solution of this base is evaporated to dryness a new base is produced, the salts of which are isomeric with those of the original series. As a difference of structure seems excluded, the two series of salts are almost certainly stereoisomeric. Vernon's observations indicate therefore that in dimethyltelluronium iodide the four radicles about the tellurium atom have not a regular tetrahedral arrangement as might have been anticipated, but lie more or less in one plane.



According to this view the α -salts and α -base are *trans*-compounds, the β -salts are *cis*-compounds, and the displacement of the methyl groups on heating the α -base is due to the fact (for which some experimental evidence was obtained) that the β -base is an oxide. The marked analogy which this formulation indicates between the configurations of the dimethyltelluronium iodides and those of platosemiamminochloride and platosemiamminochloride as interpreted by Werner is very suggestive.



This work, the results of which are published in four papers in the Society's *Transactions* (T., 1920, 117, 86, 889; this vol., p. 105,

687), occupied Vernon until Christmas. For it he was awarded the certificate of research of the University and in due course took his B.A. degree.

During the Christmas vacation, which he spent at Montreux, he was attacked with another serious illness, and in consequence had to undergo a severe abdominal operation, so that he was unable to return to Cambridge until Easter, 1920. He was then appointed to the official position in the University of Assistant to the Professor of Chemistry and began, in conjunction with Sir William Pope and Mr. F. G. Mann, a detailed experimental investigation of the interaction of ethylene and sulphur monochloride (this vol., p. 634). During the next few months his health, to external appearances, improved greatly, and he seemed to have made a complete recovery from the operation at Montreux, but in the late autumn disturbing symptoms of arterio-sclerosis, brought about by the kidney disease left as a consequence of his early illness, showed themselves and increased in gravity through the early months of the present year. He sank very rapidly at the end and died on April 9th, 1921, at the age of thirty-six.

Although Vernon had been at Cambridge for comparatively so short a time, he had gained the affectionate regard of many of the senior members of the University as well as of the younger men, for his personality was one of singular charm and attractiveness that rapidly won the friendship of all with whom he was more closely associated. His education had been so different from that of the men whom he met in the laboratories and colleges as to give him a fresh and often unconventional outlook on the questions that arose, and the engaging frankness with which he would state his views made him always an interesting companion.

As a chemist he was gifted with quite exceptional experimental skill. All who were familiar with his methods of work were greatly impressed with his powers and know that through his untimely death an investigator of unusual promise has been lost.

W. H. M.

Organic Chemistry.

Petrol prepared from Rape Oil. ALPHONSE MAILHE (*Compt. rend.*, 1921, **173**, 658—660).—When rape oil is passed over a copper-aluminium catalyst at 550—650°, it gives a gas, burning with a very luminous flame and consisting of olefins and paraffins, together with some carbon monoxide and dioxide, and a liquid from which two fractions can be obtained by distillation. If these two lighter fractions are hydrogenated over reduced nickel at 180°, they give a mixture of aromatic and cyclic hydrocarbons.

W. G.

Hydrogenation of Acetylene for the Preparation of Fuel Oils. KENJI ODA (*J. Chem. Ind. Japan*, 1921, **24**, 1161—1166).—The catalyst was prepared by reducing a mixture of nickel and mercury oxides in a current of hydrogen. Over this catalyst a mixture of equal volumes of purified acetylene and hydrogen was passed slowly at 25—35°. A light oil, consisting of ethylenic hydrocarbons, and a heavy oil, b. p. 200—300°, which remained with the catalyst, were obtained, the total yield being 51.7% of the acetylene.

K. K.

Preparation of Tetrachloroethane and Trichloroethylene from Acetylene and Chlorine. SADAŌ IGI (*J. Chem. Ind. Japan*, 1920, **23**, 1217—1237).—For the preparation of tetrachloroethane from acetylene and chlorine, the use of antimony pentachloride as a catalyst is desirable, but difficulties arise in the decrease of the absorptive power of the catalyst, in its recovery, and in the danger of explosions. Trichloroethylene is prepared in 84% yield by boiling tetrachloroethane (100 parts) with calcium hydroxide (60 parts) and water (50 parts).

CHEMICAL ABSTRACTS.

Preparation of Methyl Bromide. WILHELM STEINKOPF and GUSTAV SCHWEN (*J. pr. Chem.*, 1921, **102**, 363—364).—The addition of bromine to a mixture of phosphorus and methyl alcohol at the ordinary temperature (Steinkopf and Frommei, A., 1905, i, 501) sometimes results in the production of flame. This danger may be avoided and the yield of methyl bromide, calculated on the bromine used, increased to 77% if the methyl alcohol is boiled for about fifteen minutes before the addition of bromine and gentle boiling maintained while the bromine is being added. Methyl bromide is thus obtained far more cheaply than by Bygdén's method (A., 1911, i, 413).

T. H. P.

The Dimorphism of Potassium Ethyl Sulphate. DALZIEL LEWELLYN HAMMICK and JOHN MYLNE MULLALY (T., 1921, **119**, 1802—1806).

VOL. CXX. i.

ii

The Liver Lecithin. P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1921, **48**, 185—196).—Liver lecithin, purified by means of the cadmium chloride compound, yields on hydrolysis two saturated and two unsaturated fatty acids. The former are palmitic and stearic acids, whilst, of the latter, one gives stearic and the other arachidic acid on reduction. The degree of unsaturation of the unsaturated acids has not been determined; the one yielding arachidic acid on reduction appears, however, to form an octabromide. The presence of four different acids suggests that liver lecithin is a mixture of different lecithins. This is confirmed by molecular-weight determinations of hydrolecithin, $C_{44}H_{90}O_9NP$, obtained by Paal's method, for which the boiling-point method yielded values of 810 and 700 (cf. A., 1920, i, 788). E. S.

Preparation of Methyl Mercaptan. F. ARNDT [with E. MILDE and G. ECKERT] (*Ber.*, 1921, **54**, [B], 2236—2242).—*S*-Methylisothiobarnide sulphate, needles, m. p. 244° (decomp.), is prepared conveniently in about 90% yield by gently warming an aqueous solution of thiobarnide with methyl sulphate until the first violence of the action subsides and subsequently evaporating the solution until most of the solvent is eliminated. It is decomposed when warmed with 5*N*-sodium hydroxide solution into cyanamide (which immediately becomes polymerised to dicyanodiamide) and methyl mercaptan, which is obtained pure after being washed with a little dilute sulphuric acid and dried with calcium chloride; methyl mercaptan has b. p. 6° , d_4^{20} 0.894.

S-Methylisothiobarnide, $SMe \cdot C(NH) \cdot NH_2$, is readily prepared by the action of methyl mercaptan on cyanamide in well-cooled, anhydrous ether; it crystallises in colourless leaflets, m. p. 79° after softening at 75° , becoming decomposed thereby into methyl mercaptan and dicyanodiamide. It can be preserved unchanged in closed vessels in an ice-chest for one to two days, but gradually becomes decomposed with formation of dicyanodiamide. Previous failures to isolate the compound from its salts are not due to inherent instability of the substance, but to the use of solvents of unsuitable boiling-point; the isolation is conveniently effected from the hydrochloride and sodium methoxide in absolute methyl alcoholic solution. H. W.

Some Derivatives of Monothioethylene Glycol. GEORGE MACDONALD BENNETT and EDITH MURIEL WHINCOP (*L.*, 1921, **119**, 1860—1864).

Dichloroacetates and Chlorobromoacetates from α , β -Dichlorovinyl Ethyl Ether. HOLLAND CROMPTON and PHYLLIS MARY TRIFFITT (*L.*, 1921, **119**, 1874—1875).

Anhydrides of the Higher Aliphatic Fatty Acids. D. HOLDE and IDA TACKE (*Chem. Zeit.*, 1921, **45**, 949—950; 954—956; cf. Holde and Smekus, A., 1920, i, 811; Holde and Tacke, A., 1920, i, 811).—The pure anhydrides of the fatty acids of linseed oil can be prepared in 92.4% yield by heating the mixed fatty acids

with two and a half times the theoretical quantity of acetic anhydride at 140–160°, removal of acetic acid and unchanged acetic anhydride by distillation of the product from a boiling-water bath under 14 mm. and finally under 1–2 mm. pressure, agitation of the solution of the residue in light petroleum with sodium carbonate solution (4%) to which alcohol is ultimately added, and removal of the solvent in a current of carbon dioxide, and, finally, in a vacuum. When exposed to air, the anhydrides dry less rapidly than the corresponding glycerides, but suffer a greater increase in weight owing to hydration to the corresponding acids and oxy-acids. Pure oleic anhydride crystallises in silvery scales, m. p. 22.2°, and can be used for certain culinary operations. Its electrical conductivity in anhydrous acetone is considerably greater than that of oleic acid; glacial acetic acid is not a suitable solvent for this purpose, since it is partly converted into acetic anhydride under the influence of oleic anhydride.

The behaviour of the anhydrides when heated under diminished pressure has been investigated in the case of the compounds from rape-seed oil; under 22 mm. pressure, about 30% distils over and the residue then suddenly becomes transformed into a porous, rubber-like mass probably consisting of polymerised substances which are convertible only with difficulty into the corresponding fatty acids.

Hanus's method is strongly recommended for the estimation of the iodine numbers on account of its accuracy and rapidity. H. W.

Metal Salts of Thioglycollic [α -Thiolacetic] Acid. C. N. MYERS (*J. Lab. Clin. Med.*, 1921, 6, 359–373).— α -Thiolacetic acid is prepared by heating chloroacetic acid with potassium hydrogen sulphide, acidifying, and extracting the free acid with ether. When the clear mixture formed by dissolving metallic salts or hydroxides in an aqueous solution of the sodium salt is acidified, acids of the type $SR\cdot CH_2\cdot CO_2H$ are obtained. These are generally crystalline substances readily soluble in water, but decomposing in aqueous solution, especially in light, with the production of a metallic sulphide. Salts of the type $SR\cdot CH_2\cdot CO_2Na$ are obtained by addition of absolute alcohol to solutions of the metallic oxides in sodium α -thiolacetate solution. Compounds of the following were prepared: bismuth, copper, rubidium, silver, gold, glucinum, cadmium, mercury, thallium, cerium, lead, vanadium, arsenic, antimony, molybdenum, tungsten, uranyl, nickel, cobalt, platinum, and zinc.

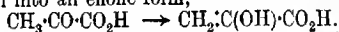
CHEMICAL ABSTRACTS.

The Significance of the Formation of Boro-complexes (and Acetonic Compounds) in Studying the Constitution and Configuration of Polyhydric Alcohols and Hydroxy-acids. J. BÖSEKEN (*Rec. trav. chim.*, 1921, 40, 553–567).—A summary of work carried out by the author and his students during the past ten years. The following conclusions are drawn: Boric acid in dilute aqueous solution forms strong complex acids with phenols and polyhydric alcohols when the hydroxyl groups are situated

in the same plane and on the same side of the two carbon atoms to which they are attached. The production of these acids is due to the formation of five-, and in some cases six-membered rings. Similar groups exert a repulsive action on each other. The chemical character of the organic portion of the complex has a minor influence on its acidity: the increase in conductivity depends primarily on the favourable position of the hydroxyl groups. The results enable the positions of the hydroxyl groups in space to be determined with respect to each other and to the rest of the molecule with greater certainty than hitherto; theoretical inferences are in accord with the facts when the mobility of molecular structure is taken into account.

The summary deals systematically with each group of organic compounds members of which have been investigated. In solution, the carboxyl group is hydrated to $C(OH)_3$, and in concentrated solution α -keto-carboxylic acids to $-C(OH)_2C(OH)_3$. H. J. E.

The Influence of some α -Keto-acids on the Conductivity of Boric Acid. J. BÖESEKEN and B. B. C. FELIX (*Rec. trav. chim.*, 1921, 40, 568—573).—The increased conductivity of boric acid in presence of pyruvic acid in concentrated solution has been attributed to the hydration of pyruvic acid or, alternatively, to its transformation into an enolic form,



The latter explanation cannot apply in the case of trimethylpyruvic acid, which gives similar results with boric acid. Three aromatic α -ketonic acids (phenylglyoxylic, mesitylgyoxylic, and phthalonic), each having no hydrogen atom attached to the β -carbon atom, have been examined for comparison. The effect varies in each case to a different amount with the concentration. The conclusion is drawn that, in concentrated solution, hydration of the CO -group, in addition to hydration of the CO_2H -group occurs, dissociation of the former taking place rapidly with dilution.

H. J. E.

The Distinction between α -Hydroxy-acids, $OH\cdot CHR\cdot CO_2H$ and $OH\cdot CRR'\cdot CO_2H$, by the Boric Acid Method and the Space Configuration of these Substances. J. BÖESEKEN (*Rec. trav. chim.*, 1921, 40, 578—581).—As the increase in conductivity in solutions of boric acid caused by the addition of α -hydroxy-acids depends on the space relation of two hydroxyl groups (see above), such increase may be used to distinguish between the two series of acids as for mono-substituted acids, it is less than for di-substituted. The influence of the hydroxyl group increases with the weight of R in the aliphatic series. In the aromatic series, other causes affect the regularity of the increase. When a hydroxyl and a carboxyl group are attached to the same carbon atom which forms part of a ring, the effect seems to decrease. Suggestions are made as to the interpretation of the results with regard to the space configuration of hydrated carboxyl groups.

H. J. E.

The Formation of Oxalic Acid from Lignin. E. HEUSER and A. WINSVOLD (*Cellulosechem.*, 1921, 2, 113).—Heuser, Roesch, and Gunkel (*Cellulosechem.*, 1921, No. 2) have stated that the alkaline fusion of lignin, prepared by Willstätter and Zechmeister's method, yields little or no oxalic acid. It is now found that a yield of 20% of oxalic acid can be obtained from lignin. Thus, 4 grams of lignin and 50 grams of potassium hydroxide are heated for forty minutes at 280°. The fused mass is dissolved in water, dilute hydrochloric acid added to precipitate unaltered lignin, and from the filtrate, after clarification with animal charcoal in the usual manner, the oxalic acid is precipitated as calcium oxalate (1.016 grams); cf. A., 1919, i, 58, 239, 368. F. M. R.

Preparation of Fumaric Acid. CARL WEHMER (Brit. Pat. 146411).—Fumaric acid is obtained by the fermentation of saccharine liquids such as beer wort, grape juice, or solutions of sucrose, dextrose, maltose, etc., containing the requisite nutritive material, with a pure culture of *Aspergillus javanicus*, otherwise known as *A. fumarius*. For example, 100 grams of sugar in 1 litre of water are sterilised and inoculated with the fungus; 35 grams of calcium carbonate and the usual nutritive salts for the fungus are added, and after two to three weeks' fermentation at 20° about 120 grams of crystalline calcium fumarate will have been deposited from the solution. From this salt fumaric acid is obtained by any of the usual methods. G. F. M.

Experiments on the Synthesis of the Polyacetic Acids of Methane. IV. Conditions of Formation by the Cyanoacetic Ester Method of Stable Methanetriacetic Esters. CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN (T., 1921, 119, 1865—1868).

Experiments on the Synthesis of the Polyacetic Acids of Methane. V. The Preparation of Carboxymethanetriacetic Acid. CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL (T., 1921, 119, 1869—1874).

Phosphoric Esters of some Substituted Glucoses and their Rate of Hydrolysis. P. A. LEVENE and G. M. MEYER [with I. WEBER] (*J. Biol. Chem.*, 1921, 48, 233—248).—The present paper is a continuation of one by Levene and Yamagawa (A., 1920, i, 712). The rates of hydrolysis of the following phosphoric esters were studied, the amorphous barium salt being employed in each case: (1) ζ -Phosphoric ester of α -, β -, γ -, ϵ -diacetone-glucose, (2) ζ -phosphoric ester of $\alpha\beta$ -monoacetone-glucose, (3) phosphoric ester of $\alpha\beta$ -monoacetone-glucose, (4) γ - or ϵ -phosphoric ester of $\alpha\beta$ -monoacetone-glucose, (5) ζ -phosphoric ester of $\beta\gamma\epsilon$ -trimethyl methyl glucoside, (6) β -phosphoric ester of $\gamma\epsilon\zeta$ -trimethyl methyl glucoside. The positions of the phosphoric acid groups, where stated, were determined by the method of preparation. (2), (3), and (4) gave hydrolysis constants of $58(10^{-3})$, $44(10^{-3})$, and $24(10^{-3})$ respectively; the rate of hydrolysis of (1) was identical, and that of (5)

almost identical, with that of (2), whilst (6) did not yield a constant, a result which was attributed to the probable presence of trimethyl glucoside as an impurity. The authors conclude from these results that the stability of the phosphoric acid group depends on its position in the sugar molecule. (6) Was prepared by the following method: $\alpha\beta$ -monoacetone-glucose was methylated by means of methyl sulphate, giving $\gamma\epsilon\zeta$ -trimethyl- $\alpha\beta$ -monoacetone-glucose, b. p. $88-90^\circ/0.03$ mm., $[\alpha]_D^{20} -28.5^\circ$. Hydrolysis of this gave $\gamma\epsilon\zeta$ -trimethylglucose, b. p. $147^\circ/0.05$ mm., $[\alpha]_D^{20} -10.95^\circ$ initial, -14.6° final, which was converted into $\gamma\epsilon\zeta$ -trimethylmethylglucoside, b. p. $135^\circ/0.035$ mm., by heating with methyl alcoholic hydrogen chloride (cf. Irvine and Scott, T., 1913, 103, 573). E. S.

The Constitution of Polysaccharides. III. The Relationship of *l*-Glucosan to *d*-Glucose and to Cellulose. JAMES COLQUHOUN IRVINE and JOHN WALTER HYDE OLDHAM (T., 1921, 119, 1744-1759).

The Thermal Decomposition of Sucrose under Reduced Pressure. JOSEPH REILLY (*J. Soc. Chem. Ind.*, 1921, 40, 249-251r).—A study of the dry distillation of sucrose under similar conditions to those which have been employed already with cellulose or starch. On an average, the yield of distillate collected at 60° was about one-quarter that obtained in comparative experiments with cellulose or starch, and was also less than that previously obtained from β -glucose or certain β -glucosides. In the dry distillation of sucrose under reduced pressure, there is much decomposition, and the distillate, after purification, appears to be a mixture which contains substances closely related to the sugars. The presence of *l*-glucosan in the mixture was established through the formation of tribenzoyl-*l*-glucosan, m. p. $198.5-200^\circ$, but the amount could represent only a small proportion of the original sucrose molecule. Assuming that the breakdown of sucrose follows similar lines to the breakdown of cellulose under similar conditions, this result indicates the absence of the β -glucose structure as a main grouping in sucrose structure. The presence of a second compound in the distillate was suspected, for a small quantity of a nitrate, white crystals, m. p. $138-145^\circ$, was isolated from the products of nitration of the purified distillate and differed from *l*-glucosan trinitrate and levulosan trinitrate.

The presence of furfuraldehyde in the distillate was shown by the formation of furfuralamide, m. p. 117° , furfurylideneacetone, m. p. $39-40^\circ$, and the *p*-nitrophenylhydrazone, m. p. $136-137^\circ$. Derivatives of furfuraldehyde were also present, but were only qualitatively studied. Acetic acid is the principal acid present in the distillate. During the thermal decomposition of sucrose under reduced pressure, gases and vapour are evolved continuously. In one experiment, formaldehyde was detected, and in other experiments, in which 99 c.c. of gas at $20^\circ/753$ mm. were obtained from 1 gram of pure sucrose, the presence of carbon dioxide, carbon monoxide, and unsaturated hydrocarbons, and a saturated hydrocarbon was observed. F. M. R.

Method of Dispersion of Cellulose in Concentrated Aqueous Solutions of Neutral Salts. P. P. VON WEIMARN (*Kolloid Zeitsch.*, 1921, 29, 197—198).—An answer to a criticism of Herzog and Beck (this vol., i, 97) of the author's work on the dispersion of cellulose in concentrated aqueous solutions of neutral salts (A., 1912, i, 679). The author points out that whilst cellulose may be dispersed in aqueous solutions of sodium iodide, calcium bromide, calcium iodide, strontium iodide, and barium, calcium, and strontium thiocyanates under atmospheric pressure, in other cases, such as solutions of sodium, potassium, and barium chlorides, increased pressure must be employed. J. F. S.

Swelling and Dispersion of Cellulose in Concentrated Aqueous Solutions. P. P. VON WEIMARN (*Kolloid Zeitsch.*, 1921, 29, 198—199).—Cellulose may be dispersed in a solution of any easily soluble salt of a sufficiently great concentration, and the degree of dispersion is so much greater the more soluble and the more hydrated the salt is. Dispersion and swelling of cellulose may also be effected by bringing it into contact with water under a large external pressure. The swelling and dispersion produced by salt solutions increase in the following order: sodium chloride, barium chloride, potassium iodide, strontium chloride, calcium bromide, and lithium chloride at ordinary temperatures and pressures. In the case of sodium chloride, the swelling is scarcely noticeable after the materials have been in contact for five years and eight months, whilst with lithium chloride complete swelling has occurred in a much shorter time. J. F. S.

Chloro-cellulose Esters, and the Action of Chloro-acyl Chlorides on Cellulose. W. LEIGH BARNETT (*J. Soc. Chem. Ind.*, 1921, 40, 253—256r).—The action of chloroacetyl chloride and also of the mixed chloroacetic-acetic anhydride on cellulose is one of esterification accompanied by resolution of the cellulose coupled with partial hydration of the cellulosic residue. The hydration occurs during the treatment of the ester with water while it is being freed from acidic impurities. More than fifty preparations were made from cellulose and chloroacetyl chloride under different conditions, and in many cases the reaction could not be checked in time to isolate solid esters insoluble in water, for, in general, rapid degradation of the complex accompanied esterification, and resulted in the formation of water-soluble esterified carbohydrates. In a typical preparation, 1 gram of cellulose was moistened with acetic acid (which just previously had been coloured by chlorine) and the excess liquid removed by squeezing; 10 c.c. of a mixture of 1 part of pyridine with 2 parts of toluene were added; and then slowly with stirring 8 c.c. of chloroacetyl chloride, containing a trace of sulphur dioxide. The cellulose gelatinised gradually, and the solution became very dark, but cleared somewhat on warming. The gelatinous mass obtained on cooling consisted of a product soluble in alcohol, cellobiose heptaacetate, and a cellulose glycollate, $[C_6H_7O_2(CO_2 \cdot CH_2 \cdot OH)_3]_7 \cdot HCl$, soluble in ether, finally obtained as a white powder, m. p. 237—238°.

The glycollic esters of cellulose were investigated further, and a large number of mixed esters, with definite melting points and great solubility in acetone, were obtained, for example,

$[(C_6H_7O_2)_3(CO_2 \cdot CH_2 \cdot OH)_7(OAc)_2]_{13} \cdot 10HCl$, a white powder, m. p. 256°. The action of dichloroacetyl chloride on cellulose in presence of pyridine, diluted with benzene, is more vigorous; the products are not uniform, but consist of cellulose acetates with chlorinated esters. The esterification of cellulose proceeds smoothly with chloroacetyl chloride in acetic acid solution together with traces of chlorine and sulphur dioxide, and the products can be isolated as required. The products all correspond with the general formula $(C_{14}H_{20}O_{10})_n HCl$, and appear to be mixed esters of acetic and hydraacrylic acids. They are powders possessing definite melting points which decrease with diminution in the value of n , whilst the chlorine content increases. When melted they form transparent liquids which solidify to almost colourless resins on cooling. For example, $(C_{14}H_{20}O_{10})_{12} HCl$, m. p. 225–226°; $[C_6H_7O_2(CO_2 \cdot CH_2 \cdot CH_2 \cdot OH)_2 \cdot OAc]_{18} \cdot HCl$, m. p. 222°, which forms a red *p*-bromophenylhydrazone, m. p. 196° with decomp.; $(C_{14}H_{20}O_{10})_{11} HCl$, m. p. 202°; $(C_{14}H_{20}O_{10})_{13} HCl$, m. p. 224–225°, which forms a benzoate, m. p. 230°; $(C_{14}H_{20}O_{10})_8 HCl$, softens at 190°, m. p. 202°; $(C_{14}H_{20}O_{10})_4 HCl$, with no definite melting point, but forms a syrup at 168°.

Attempts to prepare a similar series of products by using mixed acetic-chloroacetic anhydride, $CH_3 \cdot CO \cdot O \cdot CO \cdot CH_2Cl$, led to products of the general formula $[C_6H_7O_2(OAc)_3]_n \cdot HCl$.

At no stage in any of the series of cellulose esters, or derivatives therefrom, is there an abrupt change in properties, but throughout as the magnitude of the cellulose complex diminishes so the physical constants such as solubility and melting point become clearly defined, and also follow a general order, the solubilities increasing and the melting points decreasing with diminution of the number of cellulose units left in the esters.

F. M. R.

Investigation of the Viscosity of Cellulose Acetates. ANNA VON FISCHER (*Kolloid Zeitsch.*, 1921, 29, 260–265).—It is shown that the suitability of a cellulose acetate for the production of a plastic substance cannot be decided from its viscosity alone, but from the viscosity-composition curve. The viscosity of cellulose acetate in a series of solvents has been investigated, and the influence of temperature determined in some cases. The solvents examined were: acetone, acetone-alcohol, acetone-20% camphor, acetone-40% camphor, acetone-10% triacetin, acetone-25% dichlorohydrin, acetone-50% dichlorohydrin, and acetone-10% *p*-toluenesulphonamide. It is shown that the thirty-nine specimens of cellulose-acetate examined may be classed in seven viscosity types. A viscosity minimum in a mixture of acetone and alcohol containing 90 vol. % of acetone indicates an unusable cellulose acetate; whilst a cellulose acetate which gives a minimum viscosity in the mixed solvent containing 80 vol. % of acetone is a particularly usable specimen. Between the good type, 7, and the poor type, 1, no

difference could be found in the viscosity curves. Addition of Japanese camphor and triacetin increases the viscosity of cellulose acetate in pure acetone solution. The addition of dichlorohydrin and *p*-toluenesulphonamide increases the viscosity of solutions of the one cellulose acetate but decreases that of the other. Preliminary experiments on the viscosity of solutions of cellulose nitrate are described.

J. F. S.

Relation to Lignin of Crude Resin and Tannic Acid in Spruce Needles. A. C. VON EULER (*Svensk. Pappers-Tid.*, 1921, 24, 191—195).—A summary and extension of conclusions based on investigations by Klason (A., 1920, i, 148, 474, 821).

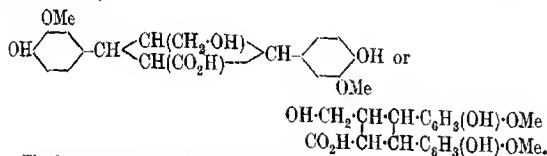
CHEMICAL ABSTRACTS.

Lignin Substance. K. H. A. MELANDER (*Svensk. Pappers-Tid.*, 1921, 24, 195—196).—Review of a dissertation by I. L. Hochfelder. By digestion of spruce chips with phenol, two substances, "lignin substance- α " (insoluble in ethyl ether) and "lignin substance- β " (soluble in ethyl ether) were obtained in the proportions of 23.1% and 18.6% respectively. The molecule of the former contains three hydroxyl groups, but no carboxyl or carbonyl groups.

CHEMICAL ABSTRACTS.

Lignin. I. Sulphite Liquor Lactone. BROR HOLMBERG (*Ber.*, 1921, 54, [B], 2389—2406).—Much of this paper has been already published (this vol., i, 25).

If, as proposed, the sulphite liquor lactone is that of diguaiacyl-tetramethylenecarbinolcarboxylic acid, the latter will have the constitution,



The lactone crystallises in small, white, six- or eight-sided plates or in flat, oblique, or wedge-shaped or triangular, pointed prisms, and in boiling acetone has the molecular weight corresponding with the formula $\text{C}_{20}\text{H}_{20}\text{O}_8$. In alcoholic solution, it gives with ferric chloride a green coloration changing to brown, and with nitrite and concentrated sulphuric acid a brown solution, becoming green and then violet. With phloroglucinol and hydrochloric acid, it gives no reaction, but an alkaline solution which has been attacked by the air gives an intense cherry-red coloration with this reagent; the liginosulphonic acids of sulphite liquors exhibit similar behaviour (cf. Klason, A., 1918, i, 59).

The corresponding hydroxy-acid separates in bundles of capillary or fine, acicular crystals; various salts are described. The amide has $[\alpha]_D^{25} + 85^\circ$, and the diacetyl derivative of the lactone $[\alpha]_D^{25} - 73.5^\circ$.

Sulphonation of the lactone and subsequent treatment with water yields a monosulphonic acid of the hydroxy-acid, $\text{C}_{20}\text{H}_{22}\text{O}_{10}\text{S}$.

which forms a crystalline powder, m. p. 172—173° (decomp.); the barium salt of this acid was analysed.

When brominated in ethereal solution at the ordinary temperature, the lactone yields: (1) a tribromo-derivative, $C_{20}H_{17}O_6Br_3$, which crystallises in small, acicular prisms united to stellar or leaf-like aggregates, sintering at about 230°, m. p. 238—240° (decomp.), $[\alpha]_D^{25} +20.5^\circ$, and (2) a tetrabromo-derivative, $C_{20}H_{16}O_6Br_4$, forming small, brownish-yellow crystals, sintering and darkening at about 255°, m. p. 260° (decomp.), $[\alpha]_D^{25} +30.9^\circ$.

When oxidised by means of various reagents, the lactone or the hydroxy-acid gives no definite compounds other than oxalic acid. The lactone withstands virtually without alteration a temperature of 220—230°, but at 250—260°, either at the ordinary, or slightly reduced, pressure, it undergoes transformation into products apparently identical with those obtained by treating the lactone either in the cold or more rapidly in the hot with sodium ethoxide. One such product, m. p. 210—211°, $[\alpha]_D^{25} +28^\circ$, contained 64.8% C and 5.9—6.1% H, and another, m. p. 210—212°, $[\alpha]_D^{25} +29^\circ$, 65.5—66.0% C, and 6.1—5.9% H; others showed the same melting points and rotatory powers as these, but varied in composition between that of the lactone and that of the acid. T. H. P.

Lignin. II. Dimethyl-sulphite-liquor Lactone. BROR HOLMBERG and MARTIN SJÖBERG (*Ber.*, 1921, 54, [B], 2406—2417).—Treatment of the lactone previously described (preceding abstract) with methyl sulphate yields its dimethyl derivative, to which the name α -dimethyl-sulphite-liquor lactone is given. This lactone, when subjected to the action of sodium ethoxide, is converted into the optically inactive β -dimethyl-sulphite-liquor lactone, which is not a racemic compound but is apparently diastereomeric with the α -compound, and may be hydrolysed to an optically active, stereochemically individual hydroxy-acid.

That portion of the ethereal extract of the sulphite liquors which is soluble in alcohol is found to contain small proportions of pyromucic and vanillic acids.

The α -dimethyl-lactone, $C_{18}H_{18}O_6(OMe)_4$, forms white, silky, capillary crystals, m. p. 179—180°, $[\alpha]_D^{25} -100.9^\circ$, $[\alpha]_D^{25} -99.2^\circ$, and, when heated in a vacuum, yields white, crystalline sublimates and a residue consisting largely of the β -compound. The corresponding hydroxy-acid, $C_{22}H_{26}O_7$, forms slender capillary crystals, m. p. 150—156° (frotting), $[\alpha]_D^{25} +38.5^\circ$, $[\alpha]_D^{25} +38.9^\circ$; various salts are described. Oxidation of the lactone in different ways yields principally oxalic acid.

The β -dimethyl-lactone, $C_{22}H_{24}O_6$, separates in flat, white needles or capillary crystals, m. p. 142—143°. The β -dimethyl-hydroxy-acid, $C_{22}H_{26}O_7$, crystallises in superimposed, colourless, rectangular plates ($+3\frac{1}{2}H_2O$), m. p. about 95° (not sharp), $[\alpha]_D^{25} +52.1^\circ$ to 52.6° . T. H. P.

Lignin. III. Alkali Lignins. BROR HOLMBERG and TEODOR WINTZELL (*Ber.*, 1921, 54, [B], 2417—2425).—The authors have

investigated the so-called black liquor obtained as waste product in the soda-cellulose process; the original wood was mainly pine, 1 part of sodium oxide being used in the extraction of 5.8 parts of absolutely dry wood, and no sodium sulphide being employed. With this liquor, sulphuric, hydrochloric, acetic, and carbonic acids gave apparently identical precipitates, which are separable by treatment with alcohol into two principal fractions: (1) α -Lignin, which is insoluble in alcohol, has a composition corresponding with the empirical formula, $C_{40}H_{42}O_{13}$, and (2) λ -lignin, soluble in alcohol and having a composition corresponding with $C_{40}H_{44}O_{12}$. Both are greyish-yellow to yellowish-brown, amorphous powders, and both readily yield colloidal solutions and behave like phenolic compounds of high molecular weight. Each contains between three and four methoxyl groups per C_{40} -complex, this number being increased to about six by treatment of the lignin with methyl sulphate. When fused with potassium hydroxide, as described by Hönig and Fuchs (A., 1920, i, 291), these lignins yield, like the ligninsulphonic acids of sulphite liquors (Melander, A., 1919, i, 473), acetic and protocatechuic acids, and also oxalic acid. Attempts to obtain definite degradation products by oxidising the lignins or by heating at low pressures have as yet been unsuccessful.

T. H. P.

Dimethylvinylamine. KURT H. MEYER and HEINRICH HOPFF (Ber., 1921, 54, [B], 2274–2282; 2942).—Dimethylvinylamine, $NMe_2CH=CH_2$, has been prepared in moderate yield by the dry distillation of neurine chloride. It fulfils the theoretical expectations of Meyer and Lenhardt (A., 1913, i, 723) and Meyer (this vol., i, 855) in that it is an exceedingly reactive product which is particularly characterised by the great readiness with which it undergoes polymerisation.

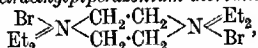
Dimethylvinylamine, a mobile liquid, b. p. $37-38^\circ$, is obtained by the dry distillation of neurine chloride, the operation being interrupted when the thermometer (in the vapour) records 80° . It readily unites with bromine in cold hydrochloric acid solution and couples with diazotised nitroaniline in acetic acid solution to an unstable orange azo-dye. It is decomposed into dimethylamine and acetaldehyde by warm dilute hydrochloric acid. The freshly-distilled base becomes completely polymerised to a white solid within twelve hours.

Neurine is prepared by the action of freshly-precipitated silver oxide on a concentrated aqueous solution of trimethyl- β -bromoethylammonium bromide and isolated as the colourless, crystalline *trihydrate* by concentration of the filtered solution in a high vacuum over phosphoric oxide at $5-10^\circ$; it is extremely hygroscopic and decomposes with great readiness when its solution is slightly warmed. When subjected to dry distillation, neurine gives a small amount of dimethylvinylamine, but is mainly decomposed into trimethylamine and vinyl alcohol, which is isolated as acetaldehyde.

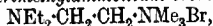
Choline has been isolated as a colourless, extremely hygroscopic,

crystalline substance which, when distilled, decomposes in all three possible directions, yielding mainly trimethylamine and ethylene glycol, with smaller amounts of β -dimethylaminoethyl alcohol and minimal quantities of dimethylvinylamine. Under similar conditions, choline chloride gives β -dimethylaminoethyl alcohol and methyl chloride.

Attempts to prepare diethylvinylamine by the following sequence of reactions are described. β -Diethylaminoethyl alcohol is transformed by hydrobromic acid (66%) at 130–135° into α -bromo- β -diethylaminoethane hydrobromide, $\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}\cdot\text{HBr}$, colourless needles, m. p. 209°, from which α -bromo- β -diethylaminoethane is obtained as a colourless liquid which readily undergoes polymerisation, b. p. 63°/0.3 mm. (In alcoholic solution it is speedily transformed into tetraethylpiperazonium dibromide,



colourless platelets or short prisms, decomp. 308°.) The action of a very large excess of pure liquid trimethylamine on freshly-distilled α -bromo- β -diethylaminoethane leads to the formation of β -diethylaminoethyltrimethylammonium bromide,



colourless, hygroscopic crystals, m. p. 208°, which is transformed by silver oxide into the corresponding crystalline ammonium base. The latter is decomposed when distilled giving minute amounts of diethylvinylamine, water, and trimethylamine and mainly methyl alcohol and α -dimethylamino- β -diethylaminoethane, a colourless liquid with a faint odour of ammonia, b. p. 156–157° (the dihydrobromide, m. p. 207–208°, platinichloride, yellow octahedra, m. p. 220°, and picrate, lemon-yellow needles, m. p. 240°, are described). α -Bromo- β -diethylaminomethane gives small quantities of diethylvinylamine when distilled with powdered potassium hydroxide. H. W.

Manufacture of Additive and Condensation Products containing Nitrogen from Acetylene and Ammonia. CHEMISCHE FABRIK RHENANIA AKT.-GES., BERNHARD CONRAD STUER, and WALTHER GROB (Brit. Pat. 147067).—Condensation products of acetylene and ammonia are obtained by passing the mixed gases in either a dry or moist condition, at normal or increased pressures, over catalysts, other than metals or metallic nitrides, such as, particularly, the oxides of iron or natural ores of iron, such as bog ore, bauxite, or chrome ironstone. The temperature of the reaction may vary within wide limits; the higher the temperature, the further the condensation proceeds. For example, at about 350° the reaction $\text{C}_2\text{H}_2 + \text{NH}_3 = \text{CH}_3\cdot\text{CN} + \text{H}_2$ predominates. Further condensation between 2 or 3 mols. of acetylene and 1 mol. of ammonia results in the formation of pyrrole and picoline respectively, and at 550° the formation of the latter substances and their homologues becomes more pronounced. For obtaining acetonitrile, the gases escaping from the contact space are cooled and the condensate is distilled, aqueous acetonitrile passing over at 72–80°. G. F. M.

The Valency Problem of Sulphur. V. Molecular Weight of Thiocyanogen. HANS LECHER and ALFRED GOEBEL (*Ber.*, 1921, **54**, [B], 2223—2229; cf. this vol., i, 414).—The instability of isolated thiocyanogen (Söderbäck, A., 1920, i, 219) renders the estimation of its molecular weight in solution a matter of difficulty. This, however, can be accomplished by the cryoscopic method by allowing a known weight of bromine to react with lead thiocyanate in the presence of bromoform, $\text{Pb}(\text{SCN})_2 + \text{Br}_2 = \text{PbBr}_2 + (\text{SCN})_2$, and measuring the depression of the freezing point thus caused. Perfectly colourless solutions are obtained which cannot contain more than traces of free bromine. Preliminary experiments show that lead bromide and thiocyanate are practically insoluble in bromoform, that the former does not combine with bromine to yield a tetrabromide, and that the latter does not unite with thiocyanogen to give a tetrathiocyanate under the experimental conditions adopted. The molecular formula of bromine in freezing bromoform is Br_2 . Even in very dilute solution, thiocyanogen shows no sign of dissociation, the molecular weight in 0.026—0.278*N* solution remaining constant and in good agreement with that required by the formula $(\text{CNS})_2$. In more concentrated solution (0.548—1.095*N*), a reversible association is observed to some extent, which is shown conclusively not to be due to incipient decomposition and consequent formation of polymerised products. It follows, therefore, that free thiocyanogen shows no analogy with the hexa-arylethanes, as suggested by Söderbäck (*loc. cit.*). The great reactivity of the substance is probably to be ascribed to the affinity of the sulphur atoms towards electrons; the substance thus falls into line with the halogens in this respect (cf. Born, A., 1919, ii, 214; 1920, ii, 156; Fajans, A., 1920, ii, 12).

H. W.

The Friedel-Crafts' Reaction. III. Migration of Alkyl Groups in the Benzene Nucleus. MATRICE COPISAROW [with CYRIL NORMAN HUGH LONG] (*T.*, 1921, **119**, 1806—1810).

Manufacture of Chlorinated Derivatives of Toluene. BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, and DOUGLAS ARTHUR CLIBBENS (*Brit. Pat.* 169025).—The chlorination in aqueous solution of toluene-*p*-sulphonic acid or its soluble salts results in the formation of 2:5-dichloro- and 2:5:6-trichloro-toluene-4-sulphonic acids, which are readily separated from one another by taking advantage of the much greater insolubility in water of the sodium salt of the trichloro-acid. If 680 grams of toluene-*p*-sulphonic acid neutralised with sodium hydroxide and dissolved in sufficient water to make about 11 litres are chlorinated until 10 c.c. of the solution have acquired an acidity equivalent to 5.5 c.c. of *N*-alkali, nearly the whole of the sodium 2:5:6-trichlorotoluene-4-sulphonate separates out in crystals, and the dichlorosulphonate is recovered in a practically pure condition by evaporating the mother-liquor. The sulphonates on hydrolysis give good yields of pure 2:5-dichloro- and 2:5:6-trichloro-toluene respectively.

G. F. M.

Manufacture of Chlorinated Derivatives of Toluene. BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, and ALFRED EDWIN HERBERT (Brit. Pat. 170056).—The chlorination of toluene-*o*-sulphonic acid or its soluble salts in cold aqueous solution results in the formation of a mixture of the 4-chloro- and 6-chloro-derivatives, which are readily separated owing to the much greater solubility of the salts of the 4-chloro-acid. Thus if a suitable concentration is selected, pure sodium 6-chlorotoluene-*o*-sulphonate separates and the mother-liquor on evaporation yields almost pure sodium 4-chlorotoluene-*o*-sulphonate, from which salts, by hydrolysis, pure 4-chloro- and 6-chloro-toluene are obtainable. By chlorinating in more dilute solution at a temperature not exceeding 60°, a mixture of dichloro- and trichloro-toluene-*o*-sulphonic acids is produced, from which the latter can easily be isolated on account of the sparing solubility in water of their sodium salts. G. F. M.

Pentabromobenzene. ALFRED ECKERT (*J. pr. Chem.*, 1921, [ii], 102, 362).—The compound, m. p. 293°, previously regarded as pure pentabromobenzene (A., 1915, i, 566), is found to be contaminated with hexabromobenzene, which is formed by the action of concentrated sulphuric acid on the pentabromo-compound. When pure, the latter has m. p. 159–160° (cf. Jacobsen and Loeb, A., 1900, i, 281). T. H. P.

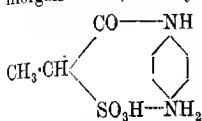
***o*-Chlorodinitrotoluenes. IV. 2-Chloro-3:4-dinitrotoluene.** GILBERT T. MORGAN and THOMAS GLOVER (T., 1921, 119, 1700–1706).

***mm'*-Dinitrodiphenylsulphone.** J. MARTINET and A. HAERL (*Compt. rend.*, 1921, 173, 775–777).—The dinitrodiphenylsulphone obtained by Gericke (*Annalen*, 1856, 100, 211) by the direct nitration of diphenylsulphone, and considered by him to be the *oo'*-, is now shown to be the *mm'*-compound. On reduction with tin and hydrochloric acid, it gives *mm'*-diaminodiphenylsulphone, m. p. 168° (cf. Gericke, *loc. cit.*), which yields a *nitrate*, a *picrate*, an *oxalate*, m. p. 175°, and a *diacetyl* derivative. When the diamine is diazotised and the subsequent solution added to boiling dilute sulphuric acid, dihydroxydiphenylsulphone, m. p. 186–187°, previously prepared by Tassinari from *p*-bromophenol (cf. A., 1887, 807; 1889, 245), is obtained. W. G.

Production of Alkylanilines. E. I. DU PONT DE NEMOURS and Co. (Brit. Pat. 145743).—Alkylanilines are obtained by heating together at a high temperature aniline, an alcohol, and a catalyst containing iodine, such as methyl iodide, hydrogen iodide, or ammonium iodide. For example, 96 parts of methyl alcohol, 93 parts of aniline, and 1.35 parts of methyl iodide may be heated in a digester at 220–240°. The liquids separate into two layers, one containing dimethylaniline, and the other the excess of alcohol used, water, and solid iodine compounds, which are recovered by distilling off the alcohol and evaporating to dryness. The residue

is likewise catalytically active, and may be employed in subsequent operations instead of methyl iodide. G. F. M.

The Action of α -Sulphopropionic Acid on some Aromatic Mono- and Di-amines. H. J. BACKER (*Rec. trav. chim.*, 1921, 40, 582—592).—The action of α -sulphopropionic acid on excess of an amine is in the first place to produce a compound by condensation of the carboxyl group of the acid with the NH_2 group, and, secondly, for the sulphonic group to react with a second molecule of the amine. The second amine molecule may be replaced by an inorganic base, and by preparing barium salts in this manner the



arylaminepropion- α -sulphonic acids may be obtained by the action of sulphuric acid. In the case of β -naphthylamine, the second molecule of the amine reacts to form a molecule of β -dinaphthylamine. Some diamines react in such a way that the second NH_2 group fulfils the same function as the second molecule of a primary amine, thus *p*-phenylenediamine forms a compound to which the annexed formula is attributed.

The following compounds have been prepared: α -Sulphopropion-anilide, $\text{SO}_3\text{H}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NHPh}$, a white, hygroscopic substance, m. p. about 205° , its aniline ester, white needles, m. p. about 255° , its sodium, barium, copper, copper ammonium, copper pyridine, and cobalt salts; the *p*-toluidine ester of α -sulphopropion-*p*-toluidide, white needles, m. p. about 251° , also the sodium salt; *p*-anisidine α -sulphopropionate, violet powder, m. p. 122° , its *p*-aniside, bluish-violet crystals, m. p. 242° . *p*-Phenetidine α -sulphopropionate, m. p. 148° , the corresponding *p*-phenetide, violet plates, m. p. 252° . β -Naphthylamine α -sulphopropionate, white substance, m. p. 203° . *p*-Phenylenediamine α -sulphopropionate, violet, crystalline powder, m. p. 210° (decomp.). α -Sulphopropion-*p*-aminoanilide, dark blue powder, m. p. 240° (decomp.). *o*-Phenylenediamine α -sulphopropionate, brown powder, m. p. 165° . Benziminazole-2-ethyl- α -sulphonic acid, $\text{C}_7\text{H}_5\text{N}_2\cdot\text{CHMe}\cdot\text{SO}_3\text{H}$, a grey, crystalline powder, benziminazole-2-sulphonic acid, small, white needles, m. p. above 300° . The formation of the last two substances, by the action of α -sulphopropionic acid on *o*-phenylenediamine, provides a simple method for the preparation of iminazole and its derivatives.

H. J. E.

Substitution Processes. KURT H. MEYER (*Ber.*, 1921, 54, [B], 2265—2273).—The remarkable reactivity of phenol in contrast with benzene has been explained by supposing it to react in the ketonic form and also by the assumption that the hydroxyl group enables it to form primary ether-like additive compounds which only pass secondarily into nuclear-substituted products. Neither theory is, however, tenable, since it is found (cf. Meyer and Lenhardt, A., 1913, i, 723) that phenolic ethers are as reactive as the phenols themselves. It appears to be a perfectly general rule that all double bonds (aliphatic, aromatic, or heterocyclic, simple or conjugated, $\text{C}=\text{C}$ or $\text{C}=\text{N}$) have increased capacity for reaction

in the presence of hydroxyl-, methoxyl-, amino-, or dimethyl-amino-groups and become "activated" towards diazo-compounds, nitrous acid, oxidising agents, halogen, etc. Phenol is therefore simply a member of a large class of products with "active double bond."

The parallelism between aliphatic and aromatic compounds is shown in the increasing reactivity in the series, ethylene, vinyl ethyl ether, dimethylaminovinylamine (Meyer and Hopff, this vol., i, 851), on the one hand, and benzene, anisole, and dimethyl-aniline, on the other.

According to the author's conception, substitution in phenols, enols, etc., is a reaction of the double bond, probably dependent on primary addition; the hydroxyl- and similar groups only play the part of activators and make the double bond more highly reactive. Evidence in favour of this view is found in the ability of aliphatic hydrocarbons to couple with diazo-compounds (Meyer and Schoeller, A., 1920, i, 97) and the extension of this reaction to aromatic hydrocarbons, for example, mesitylene (Meyer and Tochtermann, this vol., i, 895). The close connexion between ortho- and para-substitution is thus simply a case of 1:2- and 1:4-addition such as is observed frequently with aliphatic conjugated double bonds.

The hypotheses that mesitylene, aniline, and phenol show in principal similar substitution reactions leads to the conclusion that the primary action is also additive in the cases of the latter compounds. An apparent difficulty therefore arises in the interpretation of the observations that many amines, particularly aniline, and many phenols react with diazonium salts to yield compounds in which the diazo-residue is attached to the nitrogen or oxygen atom. This difficulty is removed if, for example, diazo-aminobenzene is not regarded as a necessary intermediate product in the preparation of aminoazobenzene. Evidence is adduced to show that the latter is not formed by the transformation of diazo-aminobenzene, but either by the action of the latter or of re-formed diazonium chloride on aniline. Incidentally, the formation of diazo-amino-compounds in the coupling process can be completely avoided and the operation can be conducted in such a manner as to lead directly to aminoazo-products.

The groups can be arranged in order of their increasing activation of the degree of unsaturation as follows: $\cdot\text{Me}$, $\cdot\text{OMe}$, $\cdot\text{OH}$, $\cdot\text{NH}_2$, $\cdot\text{NMe}_2$. Measurements of the rate of hydrolysis of aromatic bromo-compounds by alcoholic sodium hydroxide solution at 180° shows, as is to be expected, that the exaltation of additive capacity is paralleled by increase in the firmness of the anion of the bromine atom in the benzene ring (the experimental material comprises bromobenzene, *p*-bromotoluene, *p*-bromoanisole, *p*-bromophenol, *p*-bromoaniline, *p*-bromodimethylaniline). Conversely, the presence of groups which diminish the additive capacity, for example, NO_2 , increase the reactivity of the halogen atoms. Further, in the case of the tetra-arylhydrazines, it is to be expected that increase in the unsaturated nature of the benzene ring would increase the

dissociability; this is found to be the case, the effect of the various groups being exactly similar to that which they exert on the reactive capacity of the double bonds.

All activating groups which are attached to the terminal carbon atom of a conjugated system cause exaltation of the molecular refraction, the extent of which is exactly parallel to the chemical influence of the groups.

[With HEINRICH HOFFE and WALTER FELIX.]—*p*-Nitro-*p*'-aminoazobenzene, m. p. 137°, is formed by the addition of solid aniline hydrochloride to a solution of sodium nitrosoamine and hydrochloric acid in water. *p*-Aminoazobenzene is prepared directly by the treatment of a solution of benzenediazonium chloride in water with a concentrated aqueous solution of aniline hydrochloride. Diazoaminobenzene is converted by *m*-toluidine at 35° in the presence of a little *m*-toluidine hydrochloride into benzene-azo-*m*-toluidine, m. p. 76°. H. W.

Freezing-point Curve of *o*-Cresol-Naphthalene. F. H. RHODES and F. E. HANCE (*J. Physical Chem.*, 1921, 25, 491—494).—The freezing-point curve of the system *o*-cresol-naphthalene has been determined, and it is found that the eutectic point lies at 20.6° and the eutectic mixture contains 22.5% of naphthalene. The system is remarkable on account of the ease with which mixtures containing relatively large amounts of *o*-cresol are supercooled. So much so is this that mixtures containing far more *o*-cresol than the eutectic percentage on seeding with a crystal of naphthalene will deposit naphthalene. Such mixtures often show two "freezing points," one at which solid *o*-cresol is in stable equilibrium with the mother-liquor and a second and lower one at which solid naphthalene is in metastable equilibrium with a supercooled cresol-rich mother-liquor. J. F. S.

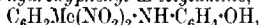
Geometrical Isomerism of *iso*Safrole. SHŌICHIRO NAGAI (*J. Coll. Eng. Tokyo*, 1921, 11, 83—100).—By gentle isomerisation of safrole with a small quantity of dilute alcoholic potassium hydroxide at 82—86°, a new unstable form of *isosafrole* was obtained, which was easily transformed into the stable form under the influence of a higher temperature and more concentrated potassium hydroxide solution. The new substance, which is shown to be a geometrical isomeride of the stable *isosafrole*, boils at 242—243°, d_4^{20} 1.1162—1.1168, and $\mu=1.5630$, all of which figures are lower, as is usual with a *cis*-isomeride, than the constants of the stable form, namely, b. p. 247—248°, $d_4^{20}=1.1230$, and $\mu=1.5730$. The two picrates also showed a difference in m. p. in the same way, namely, 68.5° and 73.5° respectively. Transformation of the *trans*. into the *cis*-form and vice versa was effected through the corresponding dibromo-additive products, which, on distillation in a vacuum, were converted into monobromo*isosafroles* with loss of a molecule of hydrogen bromide. The *trans*-form gives, of course, a *cis*-monobromo-compound and vice versa, and the latter on reduction with zinc dust and ethyl alcohol were reconverted into *isosafroles*, thus completing the cycle. Confirmation of the provisionally assigned

structure of the two *isosafoles* was obtained in the different behaviour of the monobromo*isosafoles* towards alcoholic potassium hydroxide. The above designated *cis*-monobromo-compound readily lost a further mol. of hydrogen bromide with the formation of piperonylallylene, whereas the monobromo-compound derived from the unstable *cis*-*isosafole* required a much higher temperature and a large excess of potassium hydroxide. Oxidation of both *cis*- and *trans*-*isosafole* with potassium dichromate or with ozone gave practically identical yields of piperonal from either isomeride, namely, about 35% with dichromate, and 67–69% with ozone. *cis*- and *trans*-*isosafole* dibromides were prepared by bromination in carbon disulphide solution. They were identical in properties except in optical rotation, and became turbid on keeping owing to the liberation of hydrogen bromide. For the *cis*-dibromide $[\alpha]_D^{25} +13.35$, and for the *trans*-compound $[\alpha]_D^{25} +4.45$. *trans*-*Bromoisosafole* has d 1.442, μ_D^{25} 1.555, b. p. 155–156°/20 mm., and does not become turbid on keeping. *cis*-*Bromoisosafole* has d 1.4532, μ_D^{25} 1.598, and b. p. 169–170°/19 mm. Like the dibromides, it becomes turbid on keeping, and with alcoholic potassium hydroxide at 70°, it is converted into piperonylallylene, white crystals, m. p. 41–42°, b. p. 249–251°, having a fragrant odour, and giving an intense violet coloration with sulphuric acid, and red with nitric acid.

G. F. M.

Aromatic Nitro-derivatives. XV. Substitution in the Benzene Nucleus. MICHELE GIUA and MARIO GIUA (*Gazzetta*, 1921, **51**, ii, 169–173; cf. this vol., i, 556).—The authors have investigated the behaviour of 2 : 4 : 5-trinitrotoluene towards the three aminophenols and the three aminobenzoic acids. In each case one nitro-group of the trinitrotoluene is eliminated as nitrous acid, a diphenylamine derivative being formed. The action of β -(2 : 3 : 4-) trinitrotoluene on *o*-aminophenol and on *p*-aminoacetophenone has also been studied.

4' : 6'-Dinitro-2-hydroxyphenyl-*m*-tolylamine,



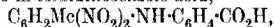
obtained from 2 : 4 : 5-trinitrotoluene and *o*-aminophenol, crystallises in lustrous, red or yellowish-brown lamellæ, m. p. 202–203°, and dissolves in alcohol to a deep red solution, and in sulphuric acid to a solution which gradually turns blue. Its *acetyl* derivative, $\text{C}_{15}\text{H}_{13}\text{O}_6\text{N}_3$, forms lustrous, yellow needles, m. p. 132°, and dissolves in sulphuric acid, giving a deep blue solution.

4' : 6'-Dinitro-3-hydroxyphenyl-*m*-tolylamine, $\text{C}_{13}\text{H}_{11}\text{O}_5\text{N}_3$, from 2 : 4 : 5-trinitrotoluene and *m*-aminophenol, forms garnet-red, prismatic crystals, m. p. 197–198°, gives a violet solution in concentrated sulphuric acid and an alcoholic solution turned deep red by addition of alkali. The *acetyl* derivative, yellow needles, m. p. 122°, forms a violet coloration with concentrated sulphuric acid.

4' : 6'-Dinitro-4-hydroxyphenyl-*m*-tolylamine, from 2 : 4 : 5-trinitrotoluene and *p*-aminophenol, was obtained by Reverdin and Crépieux (A., 1900, i, 638), and its *acetyl* derivative by Reverdin, Dressel, and Delétra (A., 1904, i, 580).

2' : 6'-Dinitro-2-hydroxyphenyl-*m*-tolylamine, $C_{13}H_{11}O_5N_3$, obtained from 2 : 3 : 4-trinitrotoluene and *o*-aminophenol, forms garnet-red prisms, m. p. 144—145°, and dissolves in concentrated sulphuric acid to a violet-red solution.

o-4' : 6'-Dinitro-*m*-toluidinobenzoic acid,

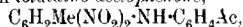


from 2 : 4 : 5-trinitrotoluene and anthranilic acid, crystallises in reddish-yellow needles, m. p. 244—245°, gives a pale yellow solution in sulphuric acid, and yields an alcoholic solution coloured reddish-brown by alkali.

m-4' : 6'-Dinitro-*m*-toluidinobenzoic acid, $C_{13}H_{11}O_6N_3$, from 2 : 4 : 5-trinitrotoluene and *m*-aminobenzoic acid, forms yellow prisms, m. p. 247—248°, and gives a reddish-brown coloration with alkalis.

p-4' : 6'-Dinitro-*m*-toluidinobenzoic acid, $C_{14}H_{11}O_6N_3$, crystallises in orange-yellow needles, m. p. 269—270°, and gives a pale yellow coloration with concentrated sulphuric acid.

p-2' : 6'-Dinitro-*m*-toluidino-acetophenone,



prepared from 2 : 3 : 4-trinitrotoluene and *p*-aminoacetophenone, forms lustrous, garnet-red prisms, m. p. 178°, gives a red solution with concentrated sulphuric acid, and yields deep reddish-brown salts with alkalis.

T. H. P.

Sulphoacetic Acid as Condensing Agent. II. Synthesis of Tri-*p*-anisylbenzene from Anisole.

WILHELM SCHNEIDER and FRITZ SEEBACH (*Ber.*, 1921, **54**, [B], 2298—2302; cf. Schneider and Meyer, this vol., i, 680).—The course of the reaction between anisole and acetic anhydride in the presence of sulphoacetic acid depends greatly on the relative proportions of sulphuric acid and acetic anhydride used in preparing the latter (cf. Schneider and Seebach, this vol., i, 878). With a mixture similar to that used in preparing diphenylmethylpyrylium compounds from acetophenone, anisole does not give a trace of di-*p*-anisylmethylpyrylium derivative, but yields *s*-tri-*p*-anisylbenzene and a red salt containing sulphur which has not been investigated. With suitable modification of the conditions, the new compound can also be obtained from pre-formed *p*-methoxyacetophenone; its preparation is thus analogous to that of mesitylene from acetone.

s-Tri-*p*-anisylbenzene, $C_6H_3(C_6H_4 \cdot OMe)_3$, crystallises in colourless needles, m. p. 142°. It yields a vivid green, crystalline additive compound with bromine, which, however, is highly unstable at the atmospheric temperature. It is transformed by hydrochloric acid at 160° into *s*-tri-*p*-hydroxyphenylbenzene, m. p. 229°, which yields a triacetate, colourless, coarse needles, m. p. 154°. H. W.

A New Phenol in the Essential Oils of the *Leptospermum*.

A. R. PENFOLD (*Perf. and Essent. Oil Rev.*, 1921, **12**, 336).—The essential oil obtained from the leaves and terminal branches of *Leptospermum flavesens* contains a phenolic substance varying

in amount from about 1–8%, according to the locality from which the material was collected. The phenol, extracted and purified in the usual way, forms an almost colourless, viscous liquid, possessing a pleasant odour, and giving with ferric chloride in alcoholic solution a brilliant orange-red coloration, and with copper salts an intense blue. It has the following characters: b. p. 145–146°/10 mm., 275–278°/770 mm., $d_{20}^{20}=1.073$, $\mu_{20}=1.5000$, optically inactive. Its composition* appears to be represented by the formula $C_{14}H_{20}O_4$, but as no solid crystalline derivatives could be obtained the accuracy of this formula could not be further tested. The phenol, to which the name *leptospermol* is given, strongly resembles tasmanol, a constituent of certain eucalyptus oils, in many of its properties.

G. F. M.

The Valency Problem of Sulphur. VI. The Sulphur Analogues of the Aromatic Diazonium Compounds. HANS LECHER and KURT SIMON (*Ber.*, 1921, 54, [B], 2249–2251).—A sulphur analogue, $Ar-S_2X$, of the aromatic diazonium compounds is obtained when *o*-nitrothiolbenzene is allowed to react in anhydrous ethereal solution at a low temperature with sulphur dichloride. After removal of a small amount of insoluble by-product, the solution is slowly evaporated under diminished pressure over calcium chloride, and the residue is freed from traces of sulphur chlorides by preservation in a vacuum in the presence of antipyrine. The compound, $C_6H_4O_2NS_2Cl$, forms yellow, well-defined crystals, m. p. 62–63° after softening at 55°. It is rapidly decomposed by moist air with the formation of hydrogen chloride. It has a normal molecular weight in freezing benzene. The question of the nomenclature of this and similar compounds is left undecided until the actual analogy of the substances with the diazonium compounds has been examined experimentally.

H. W.

The Molecular Transpositions in the Series of Alkylhydrobenzoins and of the Analogous α -Glycols. (MILLÉ) JEANNE LÉVY (*Bull. Soc. chim.*, 1921, [iv], 29, 865–878; cf. this vol., i, 233; Tiffeneau and Orékhoff, this vol., i, 243, 565, 566).—In further consideration of the dehydration of aromatic trisubstituted α -glycols, it is suggested that, with dilute sulphuric acid, the reaction is unimolecular, there being no formation of an intermediate product. The dehydration of the same glycols with concentrated sulphuric acid, or in certain cases with phosphoric oxide, will be, at least for the part of the reaction which accompanies the transposition, a bimolecular reaction resulting in the intermediate formation of diethylenic oxides. These oxides, by direct rupture or rupture consecutive to the addition of the reagent, will be transformed into transposed ketones.

These views find support in the behaviour of $\alpha\beta$ -diphenylpropan- $\alpha\beta$ -diol and of $\alpha\beta$ -diphenylbutan- $\alpha\beta$ -diol towards sulphuric acid of different strengths, it being possible in each case to isolate the intermediate diethylenic oxide and subsequently to convert it into the ketone.

W. G.

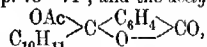
Some Retropinacolic Transpositions and the Mechanism of these Transpositions. (Mlle) JEANNE LÉVY (*Bull. Soc. chim.*, 1921, [iv], 29, 878—899).—A more detailed account of work already published (this vol., i, 233). W. G.

Studies of Halogenohydrins and Related Derivatives in the Cinnamic Acid Series. I. JOHN READ and ALBERTA CATHERINE PRITCHARD ANDREWS (*T.*, 1921, 119, 1774—1786).

The Influence of Boric Acid on the Conductivity of Phenol-carboxylic Acids. J. BÖESEKEN and (Mlle) P. OUWEHAND (*Rec. trav. chim.*, 1921, 40, 574—577; cf. this vol., i, 843).—The increase in the conductivity of *o*-hydroxy-aromatic acids brought about by adding a solution of boric acid is very great. It may be used to distinguish these acids from their isomerides, whatever the number of hydroxyl groups and their positions with respect to each other. H. J. E.

***m*-Dithiobenzoic Acid.** SAMUEL SMILES and JESSIE STEWART (*T.*, 1921, 119, 1792—1798).

***o*-Tetrahydro- β -naphthoylbenzoic Acid, its Reduction and Condensation Products.** G. SCHROETER (*Ber.*, 1921, 54, [B], 2242—2248).—The work was undertaken with a view to the discovery of possible substitutes for the fatty acids (cf. Willstätter and Waldschmidt-Leitz, this vol., i, 667).—In consideration of the general instability of tetrahydronaphthalene in the presence of aluminium chloride, it is somewhat surprising to find that it condenses readily with phthalic anhydride in not too dilute benzene solution and in the presence of the catalyst to give a 91% yield of *o*-tetrahydro- β -naphthoylbenzoic acid, colourless needles, m. p. 153—155° (the ammonium salt is sparingly soluble in water; the methyl ester, m. p. 73—74°, and the acetyl-lactone,

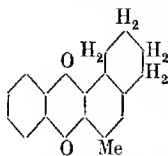


colourless needles, m. p. 135°, are described). It is reduced by amalgamated zinc and hydrochloric acid to *o*-tetrahydro- β -naphthyl-methylbenzoic acid, colourless crystals, m. p. 126°, the methyl ester of which, a colourless liquid, has b. p. 234—235°/15 mm. The latter is converted by hydrogen under pressure at 180—200° in the presence of a nickel catalyst into (?) methyl ω -decahydro- β -naphthyl-*o*-toluate, a colourless, viscous liquid, b. p. 222°/15 mm., which is transformed by hydrolysis to a semi-solid acid yielding a potassium salt with slight lathering power.

The constitution of *o*-tetrahydro- β -naphthoylbenzoic acid is deduced from the observation that it is converted by fuming sulphuric acid under certain conditions into a mixture of tetrahydronaphth-anthraquinones (2:3-compound, yellow needles, m. p. 211°, 1:2-compound, yellow needles, m. p. 135°) which are oxidised to anthraquinone-2:3- and -1:2-dicarboxylic acids respectively; the formation of the two anthraquinone compounds is only possible with a β -naphthoyl derivative, but it is remarkable that naphthalene

under similar conditions gives mainly α -naphthoylbenzoic acid (cf. Willstätter and Waldschmidt-Leitz, *loc. cit.*).

β -Methyltetrahydronaphthalene, a colourless liquid, b. p. 220—222°, prepared by the catalytic hydrogenation of β -methylnaphthalene, is converted by phthalic anhydride and aluminium chloride in



the presence of benzene into α -3-methyl-5:6:7:8-tetrahydro-2-naphthoylbenzoic acid, colourless needles, m. p. 160° (the ammonium salt is described), which is transformed by fuming sulphuric acid exclusively into the anthraquinone derivative (annexed formula), slender, yellow needles, m. p. 119°. From this observation it follows also that β -methylnaphthalene is hydrogenated in the non-methylated nucleus. H. W.

Constituents of the Kawa-root. II. Kawa Resin. W. BORSCHKE and A. ROTH (*Ber.*, 1921, 54, [B], 2229—2235).—Previous investigation of the kawa-root (*Piper methysticum*) has shown the presence of methysticin, yonganin, and a viscous, dark brown resin (cf. Borsche and Gerhardt, A., 1915, i, 438). The latter is found to consist for the most part of an ester of kawaic acid; this acid is to be regarded either as α -cinnamylideneacetoacetic acid, $\text{CHPh}:\text{CH}:\text{CH}:\text{C}(\text{Ac})\text{CO}_2\text{H}$, or γ -cinnamylideneacetoacetic acid, $\text{CHPh}:\text{CH}:\text{CH}:\text{CH}:\text{CO}:\text{CH}_2\text{CO}_2\text{H}$, and, in all probability, as the latter. The nature of the alcoholic component has not been established. Methyl or ethyl alcohol is not, however, present.

Kawa resin is decomposed under all conditions when distilled under diminished pressure, giving a yellow oil, b. p. 150—155°/13 mm., which is catalytically hydrogenated to δ -phenylbutyl methyl ketone. The resin is readily dissolved by hot, aqueous sodium hydroxide solution (10%), and the solution, when cooled, deposits sodium kawa-ate in the form of yellow leaflets. The corresponding acid, $\text{C}_{13}\text{H}_{12}\text{O}_3$, crystallises in yellow needles, m. p. 164—165°, and is readily decomposed into carbon dioxide and a dark yellow resin which yields considerable amounts of cinnamylideneacetone when distilled. Catalytic hydrogenation of sodium kawa-ate in aqueous solution according to Paal's method leads to the formation of an acid, colourless leaflets, m. p. (indefinite) above 90° (decomp.), which, however, must be almost pure tetrahydrokawaic acid, since it passes smoothly when distilled into δ -phenylbutyl methyl ketone (semicarbazone, colourless leaflets, m. p. 140—142° when rapidly heated).

Ethyl α -cinnamylideneacetoacetate differs completely from purified kawa-resin in its behaviour under the influence of warm sodium hydroxide (10%). Further, when catalytically hydrogenated and subsequently hydrolysed, it yields immediately carbon dioxide and δ -phenylbutyl methyl ketone instead of tetrahydrokawaic acid. H. W.

Replacement of the Halogen in Halogen-substituted Phthalic Acids. A. ECKERT and F. SEIDEL (*J. pr. Chem.*, 1921, [ii], 102, 338—360).—In conjunction with many collaborators,

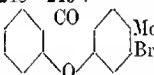
Ullmann (cf., for instance, A., 1907, i, 846) has shown that, in presence of copper, a halogen atom in an organic compound may be readily replaced by various radicles. Thus, condensation of *o*-chlorobenzoic acid with aniline or phenol leads to diphenylamine-*o*-carboxylic acid or *o*-phenoxybenzoic acid, ring closure in these compounds then yielding acridone and xanthone. The authors now find that similar replaceability is exhibited by the halogen atoms in 4:6-dibromoisophthalic and 2:5-dibromoterephthalic acids, but not by those in 3:6-dichloro-*o*-phthalic acid. The chlorine atoms in the last cannot be replaced in this manner by either phenoxy- or anilino-groups, and if they are forcibly removed by fusion of the compound with potassium hydroxide, a little water and a trace of copper, rearrangement occurs simultaneously, α -resorcylic acid and possibly protocatechuic acid being formed.

4:6-Dibromo-*m*-toluic acid, $C_8H_6O_2Br_2$, obtained by oxidation of 4:6-dibromo-*m*-xylene by means of nitric acid, forms white crystals, m. p. 174° ; its potassium salt, methyl ester, m. p. 43° , b. p. $203-206^\circ/758$ mm., and amide, $C_8H_7ONBr_2$, white needles, m. p. 188° , were prepared.

4:6-Dibromoisophthalic acid, prepared by the action of alkaline permanganate on the preceding compound, separates in needles, m. p. $250-254^\circ$, and its methyl ester in white crystals, m. p. 134° .

6-Bromo-4-phenoxy-*m*-toluic acid, prepared by heating 4:6-dibromo-*m*-toluic acid with a fused mixture of alkali hydroxide and phenol containing a little copper, forms white crystals, m. p. 137° .

6-Bromo-4-phenoxyisophthalic acid, obtained when the preceding compound is oxidised by means of alkaline permanganate, crystallises in white needles, m. p. $248-249^\circ$.

3-Bromo-2-methylxanthone, , prepared by heat-

ing the preceding acid with concentrated sulphuric acid, crystallises in white needles, m. p. 146° , and dissolves in sulphuric acid to a yellow solution showing a faint green fluorescence.

3-Bromoxanthone-2-carboxylic acid, $C_{14}H_7O_4Br$, obtained by oxidation of the bromomethylxanthone or, in better yield, from 6-bromo-4-phenoxyisophthalic acid, either by treatment with concentrated sulphuric acid or by way of the acid chloride, forms indistinct, white crystals, m. p. $338-344^\circ$, and dissolves in concentrated sulphuric acid, giving a yellow solution with faint yellowish-green fluorescence. Its methyl ester forms almost white needles, m. p. $154-155^\circ$.

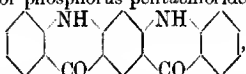
4:6-Diphenoxyisophthalic acid, prepared by heating 4:6-dibromoisophthalic acid with a fused mixture of phenol and potassium hydroxide containing powdered copper, forms crystals, m. p. $256-258^\circ$. When heated with concentrated sulphuric acid, the

acid is converted into: (1) the dixanthone, ,

which crystallises in long, pale yellow needles, m. p. 353° , and

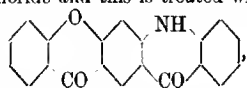
dissolves in concentrated sulphuric acid, giving a yellow solution showing marked yellowish-green fluorescence, but principally (2) a sulphonic acid of the dioxanthone, this retaining its sulphonic group with great tenacity. The dioxanthone may be more conveniently obtained by heating 4:6-diphenoxysophthalic acid with thionyl chloride; the latter usually yields only acid chlorides and rarely causes such ring-closure. When the diphenoxysophthalic acid is heated slightly above its melting point, it gives the dioxanthone and a crystalline compound, m. p. 88—96°, which was not identified. Attempts to reduce the dioxanthone resulted in no definite products.

4:6-Dianilinoisophthalic acid, $C_{20}H_{14}O_4N_2$, prepared by heating 4:6-dibromoisophthalic acid with aniline, potassium hydroxide, and copper oxide, crystallises in long, pale red needles, darkening at 265°, m. p. 270—273° (frothing), and dissolves in concentrated sulphuric acid to a colourless solution, which is coloured yellow or yellowish-brown by nitric acid and violet-red by aqueous ferric chloride; it is accompanied by another acid, possibly 6-bromo-4-anilinoisophthalic acid, but this was not investigated owing to the difficulty in purifying it. When the dianilino-acid is treated with either thionyl chloride or phosphorus pentachloride, it is converted

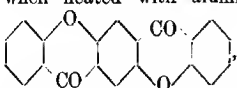
into the quinaclidone, , which crystal-

lises in yellow needles and dissolves in concentrated sulphuric acid to a violet-red solution showing red fluorescence, the colour of this liquid being discharged temporarily by aqueous ferric chloride. When kept fused for some time, the dianilino-acid loses carbon dioxide, yielding *m*-dianilino benzene.

3-Anilinoxanthone-2-carboxylic acid, $C_{20}H_{14}O_4N$, prepared by heating 3-bromoxanthone-2-carboxylic acid with aniline, forms crystals, m. p. 310—313°. When heated above its melting point, this acid loses carbon dioxide and yields 3-anilinoxanthone, $C_{19}H_{13}O_3N$, greenish-yellow needles, whilst when it is converted into the acid chloride and this is treated with aluminium chloride,

the compound, , which forms yellow crystals, is obtained.

2:5-Diphenoxysterephthalic acid, $C_{20}H_{14}O_6$, prepared from 2:5-dibromoterephthalic acid (cf. Claus and Wimmel, A., 1880, 632), separates in white crystals, m. p. 314°. Its chloride, when heated with aluminium chloride, yields the dioxanthone,

, which forms yellow crystals, and

dissolves in concentrated sulphuric acid to a red solution showing a slight blue tinge; this solution exhibits far weaker fluorescence than that of the isomeric dioxanthone.

T. H. P.

The Application of Hofmann's Reaction to Substituted Phthalimides. TOM SIDNEY MOORE, MURIEL TREGARTEN MARRACK, and ANNIE KATHLEEN PROUD (T., 1921, 119, 1786—1791).

Unsaturated Bile Acids. II. An Isomeride of apoCholic Acid. FR. BÖDECKER and H. VOLK (Ber., 1921, 54, [B], 2489—2492; cf. A., 1920, i, 848).—apoCholic acid, obtained by the action of dehydrating agents on cholic acid, is found to be accompanied by an *isomeric acid*, $C_{24}H_{38}O_4$, which crystallises in tasteless, slender, woolly needles, m. p. 259—260° (corr.), $[\alpha]_D^{25} +57.3^\circ$, decolorises bromine and permanganate, and does not appear to be a secondary product derived from apocholic acid. The barium salt (+6H₂O) was analysed, and the methyl ester, $C_{24}H_{37}O_4 \cdot Me \cdot MeOH$, forms stout prisms, m. p. 85—90° (frothing), $[\alpha]_D^{25} +60.27^\circ$, and has the normal molecular weight in boiling methyl alcohol. T. H. P.

m-Opianic Acid (4 : 5-Dimethoxy-o-aldehydobenzoic Acid). ROBERT GEORGE FARGHER and WILLIAM HENRY PERKIN, jun. (T., 1921, 119, 1724—1744).

Certain Substances contained in Lichens. G. BARGELLINI and C. MONCADA (Gazzetta, 1921, 51, ii, 173—180).—The following preliminary results have been obtained.

Stictic acid, extracted from Italian *Sticta pulmonaria* by means of acetone, agrees in properties with the acid obtained by Hesse, from the same lichen grown in Germany (A., 1898, i, 681; 1905, i, 140; 1911, i, 208), its composition being in agreement with the formula $C_{19}H_{14}O_4$. It crystallises in white needles, becomes brown at about 240°, and melts and decomposes at about 260°. In alcoholic solution, it gives a deep violet-red coloration with ferric chloride, but, unlike some other compounds occurring in lichens, it is not decomposed when heated with alcohol in a sealed tube at 150° and its alcoholic solution gives no coloration with calcium hypochlorite. Pyridine dissolves and decomposes the acid, a yellowish-red substance being formed; the action of sulphuric acid yields a red compound, that of nitric acid a yellow compound, and that of alkali carbonates a yellow, crystalline compound, m. p. 215—225° (decomp.). These various compounds are to be investigated. The acetyl derivative of stictic acid crystallises in white needles, m. p. about 230° (decomp.), but the number of acetyl groups in the molecule has not been ascertained.

Stereocaulic acid, obtained from various species of *Stereocaulon*, appears to be identical with stictic acid. T. H. P.

Citral Series. Optical Determination of the Constitution of Compounds of the Citral Series. E. KNOFVENAGEL and G. OELBERMANN (J. pr. Chem., 1921, [ii], 102, 305—331; cf. A., 1919, i, 15).—The authors have measured, for a number of citral derivatives, the refractive indices at 20° for the α -, β -, and γ -hydrogen lines and for the yellow D₃-helium line; in consequence of the tendency to undergo polymerisation and oxidation exhibited by compounds of this series, the measurements were made on liquids

freshly distilled in a vacuum. From the values obtained for the molecular refractions conclusions are drawn as to the constitutions of certain of the compounds. The effects produced on the refractive indices by storage of the compounds at -190° , -80° , or the ordinary temperature were examined.

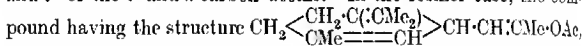
Citral, consisting of two isomerides, which are probably stereoisomerides, contains the conjugated system $\text{CR:CH}\cdot\text{CH:O}$; according to Eisenlohr (*Spektrochemie organischer Verbindungen*, 1912, 126), the latter gives the specific normal exaltation $E\Sigma_{\text{refr.}} = 1.25$ and $E\Sigma_{\text{disp.}} = 45\%$, which are in good agreement with the authors' results.

ψ -Ionone, according to Tiemann's formula for citral, contains the grouping $\text{CR:CH}\cdot\text{CH:CH}\cdot\text{CR:O}$, for which Eisenlohr (*op. cit.*, 134) gives $E\Sigma_{\text{refr.}}$ somewhat above 2.7 and $E\Sigma_{\text{disp.}}$ above 100% ; these values agree well with those now obtained. The refraction of α - and β -ionones has been investigated by Auwers and Eisenlohr (A., 1911, ii, 781, 782; cf. Eisenlohr, *op. cit.*, 127, 134).

For ψ -ionone acetate only a cyclic constitution appears possible. Taking the formula $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH:CH}\cdot\text{CO}\cdot\text{CH}_3$ for ψ -ionone, it may be assumed that the acetyl group of the acetic anhydride becomes attached to the carbonylic oxygen and the acetoxy-group to the carbon atom in the β -position, simultaneous displacement of one double linking occurring with formation of an intermediate compound of the formula



In this, the catalytic action of the ferric chloride used in preparing the compound might result in ring closure between either the γ - and δ - or the ϵ - and κ -carbon atoms. In the former case, the compound having the structure



would arise, and the theoretical exaltation for such a compound agrees best with the actual value. It is possible that isomeric ψ -ionone acetates exist, as the freshly-prepared compound boils within wide limits.

The values found for the molecular refraction of *iso*- ψ -ionone indicate the formula to be probably $\text{CH}_2\left\langle\begin{array}{c} \text{CH}_2\cdot\text{C}(\text{CMe}_2) \\ \text{CMe}=\text{CH} \end{array}\right\rangle\text{CH}\cdot\text{CH}_2\cdot\text{Ac}$,

but possibly $\text{CH}_2\left\langle\begin{array}{c} \text{CH}_2\cdot\text{C}(\text{CHMe}_2) \\ \text{CMe}=\text{CH} \end{array}\right\rangle\text{C}\cdot\text{CH}_2\cdot\text{Ac}$. The former of these two structures was attributed by Knoevenagel to α -*iso*-ionone, which, however, exhibits normal optical values.

iso- ψ -Ionone yields the same semicarbazone, $\text{C}_{14}\text{H}_{23}\text{ON}_3$, m. p. 169° , as ψ -ionone acetate.

When heated with zinc chloride at 200° , *iso*- ψ -ionone yields a hydrocarbon, $\text{C}_{13}\text{H}_{18}$, b. p. $135\text{--}145^\circ/21\text{ mm.}$, d_4^{20} 0.9373, which may have one of various structures, between which the available optical and chemical data are insufficient to decide.

Ethyl citrylideneacetoacetate (α -ester) is difficult to obtain pure, as it readily undergoes transformation into the β -ester, but the optical constants obtained indicate the probable accuracy of the structural formula already given (A., 1919, i, 15).

In the case of α -isoionone, the method of preparation and the normal optical data are in agreement with the view that the semi-cyclic double linking has somehow wandered into the nucleus, giving a compound of the constitution $\text{CH}_2 \begin{smallmatrix} \text{CH:CH} \\ \text{CMe:CH} \end{smallmatrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{Ac}.$

For ethyl β -citrylideneacetoacetate the normal optical data and the transformations into the β -iso- and the β -pseudo-esters agree best with the structure $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} : \text{C}(\text{CH}_3) \cdot \text{CH} \cdot \text{CH} \cdot \text{Ac} \cdot \text{CO}_2 \text{Et}.$

For the hydrocarbon, $\text{C}_{13}\text{H}_{18}$, obtained by the action of zinc chloride, the constitution $\begin{smallmatrix} \text{CMe} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CMe} \\ | \\ \text{CH} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CMe} : \text{CH} \end{smallmatrix}$ was proposed

(*loc. cit.*), but this is not in accord with the refractive data and the boiling point. Better agreement is shown by the structure $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \begin{smallmatrix} \text{CH:CH} \\ \text{CH-CH} \end{smallmatrix} > \text{CH}.$

The formula previously given (*loc. cit.*) for β - ψ -ionone, which exhibits normal refractive constants, is probably accurate. The same is the case with ethyl β -isocitrylideneacetoacetate, the expected absence of exaltation being virtually confirmed experimentally. Moreover, for β -isoionone, normal optical data are obtained, these being in agreement with the structure previously suggested (*loc. cit.*).
T. H. P.

The Crystalline-liquid Properties of α -Unsaturated Ketones. D. VORLÄNDER (*Ber.*, 1921, 54, [B], 2261—2264).—The crystalline-liquid properties of dianisylidenecyclohexanone recorded by Müller (this vol., i, 674) have been described previously by the author (*A.*, 1907, ii, 337; 1908, ii, 22). In the case of *pp'*-diethoxybenzylidenecyclohexanone (Huth, *Diss.*, Halle, 1909), the region of existence of the crystalline-liquid is somewhat greater, the transition points lying at 145° and 176° . In the case of derivatives of cyclohexanone, the side chain is of considerable influence, the presence of the methyl radicle having a decided hindering effect. From a considerable number of examples it is shown that the presence of the group in the para- or meta-position renders the corresponding enantiotropic forms monotropic crystalline-liquid whilst 2-methylcyclohexanone does not yield crystalline-liquid arylidene compounds. Contrary to Müller's statement (*loc. cit.*), dianisylidenecyclopentanone gives an anisotropic melt.

In general, the crystalline-liquid properties of α -unsaturated ketones are not very marked, as is shown by the relatively small regions of existence of the enantiotropic forms and the absence of the phenomenon in the benzylidene and cinnamylidene derivatives. Comparison of arylidene cyclic ketones with non-cyclic α -unsaturated ketones (which are never or but very seldom crystalline-liquid) shows that the presence of the ring enhances the crystalline-liquid properties and that the six-membered ring has a greater influence than that composed of five atoms. It is remarkable that meta-compounds are found among the cyclic derivatives, whereas crystalline-liquid derivatives of aromatic meta-substitution products in the middle of an extended molecule have not yet been observed.

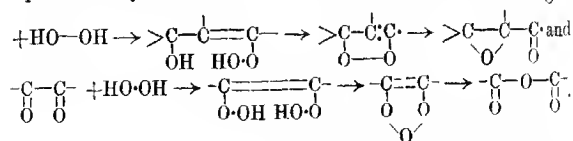
Only when the central portion of the molecule is very strongly developed linearly, for example, in *pp'*-derivatives of diphenyl and in *pp'*-diaminoazo-compounds, can almost any meta- or ortho-substituent be introduced into the molecule without completely destroying the crystalline-liquid condition.

Studies in the *n*-Butyl Series. I. Aryl *n*-Propyl Ketones.
GILBERT T. MORGAN and WILFRED JOHN HICKINBOTTOM (T., 1921,
119, 1879—1893).

Action of Alkaline Hydrogen Peroxide on Unsaturated Compounds. ERNST WEITZ and ALFRED SCHEFFER (*Ber.*, 1921, 54, [B], 2327-2344).—It has been shown previously (Weitz, *A.*, 1919, i, 290-291) that 9-benzylideneanthrone and 1:2-diphenylindene-3-one are converted by hydrogen peroxide in the presence of sodium hydroxide solution into colourless oxides. A similar, extremely ready reaction occurs with $\alpha\beta$ -unsaturated ketones; the initial product, if isolable, has the composition ketone + 1 atom of oxygen, and the identity of the substances obtained from benzylideneacetophenone, *p*-chlorobenzylideneacetophenone, and *p*-nitrobenzylideneacetophenone with the products obtained by Widman (*A.*, 1913, i, 1220; 1916, i, 406), Bodfors (*A.*, 1917, i, 223), and Jörländer (*A.*, 1917, i, 222) by the action of the substituted benzaldehydes on ω -bromoacetophenone leaves no doubt that they are substituted ethylene oxides. Alkaline hydrogen peroxide solution does not appear to react with the carbonyl or ethylene group alone, but with the combination of the two in the conjugated system, $\text{C}=\text{C}-\text{C}=\text{O}$, as it occurs in unsaturated ketones or aldehydes. $\alpha\beta$ -Unsaturated acids are relatively stable towards the reagent.

The observations have been extended to other substances containing conjugated bonds. Diolefines and substances such as sorbic acid do not exhibit any striking reactivity. 1:2-Diketones, on the other hand, react very readily, passing directly into the corresponding acids without permitting isolation of the oxide formed intermediately. α -Keto-carboxylic acids, on the other hand, are relatively stable. The course of the reactions is probably

represented by schemes such as the following:

$$\text{>C}=\overset{\cdot}{\underset{\cdot}{\text{C}}}-\overset{\cdot}{\underset{\cdot}{\text{C}}}-$$


All the ketoxido-compounds have the property of liberating iodine from potassium iodide and acetic acid with re-formation of the unsaturated ketone. In general, also, they give intensely brownish-yellow solutions when heated to boiling with aqueous alkalis which yield almost colourless precipitates when acidified; the

latter re-dissolve in alkali hydroxide solutions, yielding the original colorations.

The following individual substances are described: β -acetyl- α -phenylethylene oxide, $\text{PhCH} \cdot \text{CHAc}$, colourless leaflets, m. p. 52–53°, obtained together with a liquid isomeride from benzylideneacetone in aqueous methyl-alcoholic solution; β -benzoyl- α -phenylethylene oxide (cf. Widman, *loc. cit.*), colourless leaflets, m. p. 90°; β -benzoyl- α -*p*-nitrophenylethylene oxide, colourless leaflets, m. p. 150° (Bodforss, *loc. cit.*, gives 148°); β -benzoyl- α -*p*-chlorophenylethylene oxide, colourless needles, m. p. 80–81° (Bodforss, m. p. 79–80°); β -benzoyl- α -*o*-chlorophenylethylene oxide, crystalline aggregates, m. p. 77° (from *o*-chlorostyryl methyl ketone, pale yellow crystals, m. p. 52–53°); β -benzoyl- α -*p*-methoxyphenylethylene oxide, colourless leaflets, m. p. 87°; α -acetyl- β -methylpropylene oxide, b. p. 44–48°/15 mm.; β -benzoyl- α -styryl-ethylene oxide, $\text{CHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{Bz}$, colourless needles, m. p. 89°;

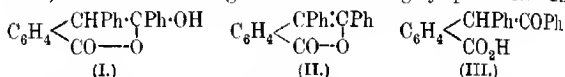
1:2-diphenylindene-3-one oxide, $\text{C}_6\text{H}_5 \cdot \text{C}(\text{CPh})_2 \cdot \text{CPh}$, short needles, m. p. 141° after becoming red at 130°; terephthalylideneacetophenone dioxide, $\text{C}_6\text{H}_4(\text{CH} \cdot \text{CHBz})_2$, leaflets, m. p. 195° after softening at 175° [Bodforss (A., 1918, i, 229) gives m. p. 220–222°, the difference being probably due to the existence of *cis-trans*-isomerism]; diphenylbenzocycloheptadione dioxide (annexed formula), prisms, m. p. 167–168°. H. W.

Transformations of Ketoxido-compounds. Formation of β -Ketonic Aldehydes from $\alpha\beta$ -Unsaturated Ketones. ERNST WEITZ and ALFRED SCHEFFER (*Ber.*, 1921, 54, [B], 2344–2353; cf. preceding abstract).—The action of acetic acid and mineral acid on ketoxido compounds leads in certain cases to the production of β -ketoaldehydes, but in more complex instances its exact course has not been fully elucidated. It is shown, however, to depend to some extent on the nature of the mineral acid used.

β -Acetyl- α -phenylethylene oxide, $\text{O} \cdot \text{C}(\text{CHPh})_2$, is converted by a solution of hydrogen chloride in glacial acetic acid into an oily chlorohydrin which slowly evolves hydrogen chloride spontaneously at the atmospheric temperature and passes into α -phenylacetaldehyde, $\text{CHPhAc} \cdot \text{CHO}$, or, more probably, hydroxymethyl-enebenzyl methyl ketone, $\text{OH} \cdot \text{CH} \cdot \text{CPh} \cdot \text{COMe}$, m. p. 67–68°. The substance is somewhat unstable at the atmospheric temperature, gives an intense, reddish-violet coloration with ferric chloride, a greenish-yellow, crystalline copper salt, and a (?) phenylhydrazone, $\text{C}_{18}\text{H}_{16}\text{ON}_2$, almost colourless, ill-defined leaflets, m. p. 171°. β -Benzoyl- α -phenylethylene oxide gives only ill-defined products with acetic acid and hydrogen chloride, but is transformed by acetic and concentrated sulphuric acids into formyldeoxybenzoin

(Wislicenus and Ruthing, A., 1911, i, 303). The transformation $O \begin{smallmatrix} \text{CHPh} \\ \diagup \\ \text{CHBz} \end{smallmatrix} \rightarrow \text{CHPh} \cdot \text{Bz} \cdot \text{CHO}$, is thus analogous to the pinacol transformation or, more precisely, to the conversion of hydrobenzoin into diphenylacetaldehyde. If the terminal carbon atom of the oxide group is not attached to a hydrogen atom, as in $\alpha\alpha$ -dimethyl- β -acetylene oxide, a 1:2-diketone appears to be formed.

1:2-Diphenylindene-3-one oxide, $\begin{smallmatrix} \text{C}_6\text{H}_4 \cdot \text{CPh} \\ \diagup \\ \text{CO} - \text{CPh} \end{smallmatrix} > \text{O}$, is converted by hydrogen chloride or hydrogen bromide and glacial acetic acid into a "hydrate," $\text{C}_{21}\text{H}_{16}\text{O}_3$, m. p. 160–168° after darkening at about 155°, or a mixture of this substance and the corresponding lactone, $\text{C}_{21}\text{H}_{14}\text{O}_2$, is also prepared from the oxide and sulphuric and acetic acids. It is converted by aqueous alcoholic alkali hydroxide solution into the acid, $\text{C}_{21}\text{H}_{16}\text{O}_3$, leaflets, m. p. 142° (decomp.) after softening at 139°. The constitution of the hydrate (i), lactone (ii), and acid (iii) have not been placed beyond doubt, but the following formulae are highly probable. The



"hydrate" is transformed by sodium hydroxide into a neutral yellow product, $\text{C}_{21}\text{H}_{14}\text{O}_2$ or $(\text{C}_{21}\text{H}_{14}\text{O}_2)_2$, m. p. 129°, which is possibly 3:3-diphenylindan-1:2-dione. H. W.

Dinaphtha-1:7:1':7'-diquinone. GILBERT T. MORGAN and DUDLEY CLOETE VINING (T., 1921, 119, 1707–1714).

Preparation of Compounds of the Anthraquinone Series. FREDERICK WILLIAM ATTACK and GEORGE WILLIAM CLOUGH (Brit. Pat. 169732).— α -Chloro- or α -bromo-anthraquinones are converted into β -halogen derivatives by heating with concentrated sulphuric acid for some hours at about 200°. As the halogen atom always takes up the meta-position with respect to its original position, the reaction is, of course, limited to those anthraquinone derivatives in which this particular β -position is unoccupied. Further, those derivatives are excluded which are decomposed by hot sulphuric acid such as 4-chloro-1-hydroxyanthraquinone, in which case the dihydroxy-compound is produced, or 4-chloro-1-aminoanthraquinonesulphonates, in which the chlorine atom is expelled. With these exceptions, the orientating action of sulphuric acid appears to be specific and the reaction with α -halogen-anthraquinones a general one. For example: 50 parts of 1-chloroanthraquinone are heated with 920 parts of sulphuric acid (d 1.84) at 200–205° for nine hours. The reaction mixture is poured into water and the precipitated 2-chloroanthraquinone recrystallised from acetic acid. G. F. M.

Octachloroanthraquinone. ALFRED ECKERT (J. pr. Chem., 1921, [ii], 102, 361).—The action of antimony pentachloride on

anthraquinone in presence of iodine yields, in addition to the compounds already described (A., 1915, i, 565), also *octachloro-anthraquinone*, $C_{14}O_2Cl_8$, which crystallises in yellow needles, m. p. above 360° . T. H. P.

The Dibromoanthraquinone Used in the Synthesis of Alizarin. GRANDMOUGIN (*Compt. rend.*, 1921, 173, 717—718).—It is shown that the dibromoanthraquinone used by Graebe and Liebermann in their synthesis of alizarin was 2 : 3-dibromoanthraquinone. W. G.

Preparation of α -Aminoanthraquinone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 169667).— α -Aminoanthraquinone may be obtained by heating α -anthraquinonesulphonic acid with ammonia under pressure in presence of the sulphonic acid of an aromatic nitro-compound. For example, if 165 parts of potassium α -anthraquinonesulphonate, 500 parts of 24% aqueous ammonia, and 60 parts of sodium nitrobenzenesulphonate are heated for twelve hours at 160 — 165° , and the contents of the autoclave are then allowed to cool, a yield of 80% of the theoretical of pure crystalline α -aminoanthraquinone is directly obtained, and a quantity of anilinesulphonic acid may be recovered from the filtrate. G. F. M.

Derivatives of 2-Methylantraquinone. ALFRED ECKERT and GERTRUD ENDLER (*J. pr. Chem.*, 1921, [ii], 102, 332—337).—The preparation of 1-methoxy-2-methylantraquinone from 1-nitro-2-methylantraquinone according to D.R.P. 75054 is difficult, and this compound is obtainable more readily by heating 1-chloro-2-methylantraquinone with methyl alcoholic potassium hydroxide in a sealed tube at 80° . It crystallises in pale yellow needles, m. p. 152 — 153° .

1-Methoxyanthraquinone-2-carboxylic acid, $C_{16}H_{10}O_5$, prepared either by oxidising the preceding compound in acetone solution by means of permanganate or, better, by boiling 1-nitroanthraquinone-2-carboxylic acid with methyl alcoholic potassium hydroxide, forms yellow needles, m. p. 250 — 253° .

5 : 8-Dichloro-2-methylantraquinone, $C_{15}H_8O_2Cl_2$, prepared by treating 3 : 6-dichlorophthalic anhydride in toluene with aluminium chloride and heating the resulting dichlorotoluoylbenzoic acid, m. p. 160 — 161° , with sulphuric acid, crystallises in yellow needles, m. p. 242 — 244° . When oxidised with chromium trioxide and sulphuric acid, it yields

5 : 8-Dichloroanthraquinone-2-carboxylic acid, $C_{15}H_6O_4Cl_2$, which forms yellow needles, m. p. above 390° .

Tetrachlorotoluoylbenzoic acid, $C_{15}H_4O_3Cl_4$, prepared from tetrachlorophthalic anhydride, forms crystals, m. p. 142° , and when heated with fuming sulphuric acid yields an acid compound which crystallises in almost colourless needles, m. p. 281° (slight browning), has the molecular weight 403, and contains 7.6% of sulphur and 33.5% of chlorine.

5 : 6 : 7 : 8-Tetrachloro-2-methylantraquinone, $C_{15}H_6O_2Cl_4$, ob-

tained like the dichloro-compound, crystallises in yellow needles, m. p. 195—196°.

Tetrachlorobenzophenonedicarboxylic acid, $C_{15}H_4O_6Cl_4$, prepared by the action of permanganate on tetrachlorotoluoylbenzoic acid in presence of sodium carbonate, forms white crystals, m. p. 280°, and when treated with sulphuric acid undergoes condensation to 5 : 6 : 7 : 8-*Tetrachloroanthraquinone-2-carboxylic acid*, $C_{15}H_4O_4Cl_4$, which crystallises in pale yellow needles, m. p. 295—296°.

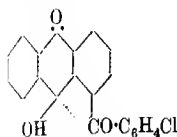
T. H. P.

New Class of Compounds with Tervalent Carbon. I. ROLAND SCHOLL (*Ber.*, 1921, 54, [B], 2376—2388).—By the action of aluminium or copper on concentrated sulphuric acid, or of zinc dust and ammonia on 1-benzoylated anthraquinones, Schaarschmidt (A., 1915, i, 566, 696; 1916, i, 408) obtained deep violet-blue compounds exhibiting pronounced fluorescence in various solvents. The author has now investigated these compounds and finds that they are not pinacones, as Schaarschmidt supposed, but representatives of a new class of compounds containing trivalent carbon.

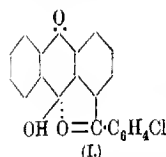
[With HERBERT HÄHLE.]—The reduction product of 1-*p*-chlorobenzoylanthraquinone, for which Schaarschmidt gave m. p. 220—222°, may be obtained crystalline in stable, curved, violet-blue needles, m. p. 253°. In solution in organic solvents it undergoes oxidation in the air and free chromic acid converts it into 1-*p*-chlorobenzoylanthraquinone. Measurements of the molecular weight in boiling nitrobenzene solution demonstrate the inaccuracy of Schaarschmidt's doubled formula. In nitrobenzene, the compound unites with bromine, the proportion of the latter combined indicating for the compound the formula $C_{21}H_{12}O_3Cl$, which is that of a compound containing trivalent carbon.

As regards the position assumed by the atom of reducing hydrogen, Schaarschmidt assumed that the addition occurred at the carbonyl of the chlorobenzoyl residue. That this is not the case and that the double ketonic group of the anthraquinone is more readily attacked by the reducing agents employed than is the carbonyl group of simple aromatic ketones is shown by the following observations. (1) Anthraquinone and many of its derivatives are easily reduced by concentrated sulphuric acid and powdered metal in the cold or at a gentle heat; thus, 1 : 1'-dianthraquinonyl yields *mesobenzdianthrone* (Scholl, Mansfeld, and Potschiwuscheg, A., 1910, i, 494). (2) When reduced by means of aluminium bronze and concentrated sulphuric acid, 2-*p*-toluoylanthraquinone yields 2-*p*-toluoyl-9-oxanthrone and 2-*p*-toluoylanthranol (Schaarschmidt and Irineu, A., 1916, i, 408). (3) 1-Benzoylallochrysoketone, which is free from the reactive quinone carbonyls, appears to yield no reduction product with concentrated sulphuric acid and powdered aluminium or copper (Schaarschmidt, A., 1916, i, 47). It is hence considered justifiable to conclude that, in the formation of the violet reduction product, $C_{21}H_{12}O_3Cl$, from 1-*p*-chlorobenzoylanthraquinone, the hydrogen atom passes to one of the quinone carbonyl groups.

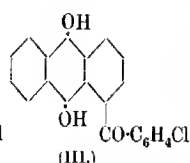
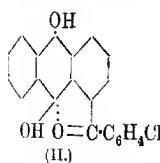
In anthraquinone derivatives with negative substituents in position 1, the carbonyl in the 9-position adjacent to the substituents appears to be more highly reactive than that in the 10-position. Thus, in the reduction of 1:1'-dianthraquinonyl to mesobenzdianthrone, the latter is obtained in almost quantitative yield. From these considerations the violet reduction product



remaining affinity of the 9-carbon atom may be largely satisfied by the residual affinity of the oxygen of the benzoyl group, with

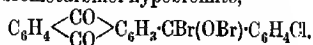


formation of the intramolecular ketone additive product shown annexed (I). Characteristic of compounds of this class is the possession of a conjugated, tervalent carbon atom co-ordinatively united in an inner complex ring. Such compounds are comparable with the additive products formed by hydrocarbons, and especially by hydroxylated aromatic hydrocarbons with ketones according to the structure given by Pfeiffer, or with the quinhydrones. As regards the behaviour of the chlorobenzoyloxanthronyl towards alkaline hyposulphite (Schaarschmidt, *loc. cit.*), it may be assumed that one hydrogen atom is taken up without rupture of the co-ordinative linking or opening of the complex ring. The resulting inner-complex chlorobenzoylanthraquinol (II) reverts



to the blue compound (I) in the air but in the alkaline solution undergoes dissociation, completely but less slowly than it is formed, into the stable "open" chlorobenzoylanthraquinol (III), which is

oxidised in the air to 1-*p*-chlorobenzoylanthraquinone. The reaction of the compound with three atoms of bromine is readily explained by the co-ordination formula. The co-ordinative linking is broken down by addition of 2 bromine atoms, the liberated principal valency of the carbon of the original chlorobenzoyl carbonyl being then saturated by the third bromine atom, with formation of a bromocarbonyl hypobromite,



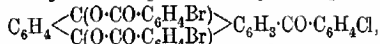
comparable with the alkyl hypochlorites.

The benzoyloxanthronyls are oxymethyls and, as they correspond

with Schlenk's metal ketyls (A., 1913, i, 1205), may be designated hydroketyls. Their discovery and stability dispose finally of Schmidlin's conception of the metal ketyls as loose additive compounds of the metals with ketones analogous to the coloured molecular compounds of ketones with metallic chlorides ("Das Triphenylmethyl," 1914, 186).

With *p*-benzoquinone the bluish-violet chlorobenzoyloxanthronyl forms an additive compound which crystallises in faintly yellow, rhombohedral plates, is comparable with the quinol bis-triphenylmethyl ether obtained by Schmidlin, Wohl, and Thommen (A., 1910, i, 377) from triphenylmethyl and *p*-benzoquinone, and in solution dissociates into its constituents below 100°, giving the characteristic colour of the chlorobenzoyloxanthronyl.

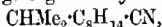
1-*p*-Chlorobenzoyl-9 : 10-di-*p*-bromobenzoylanthraquinol,



prepared by treating either 1-*p*-chlorobenzoyl-9-oxanthronyl or 1-*p*-chlorobenzoylanthraquinone in alkaline sodium hyposulphite solution under hydrogen with ethereal *p*-bromobenzoyl chloride (cf. Scholl, Mansfeld, and Potschiwawscheg, *loc. cit.*), forms a pale brown powder.

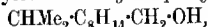
T. H. P.

The Products of Reduction of Dimethylcampholamide. A. HALLER and (MME) P. RAMART (*Compt. rend.*, 1921, 173, 682—685).—When reduced by sodium in absolute alcohol, dimethylcampholamide gives a small amount of dimethylcampholylamine together with an indefinite compound, which, during purification, undergoes dehydration, giving dimethylcampholnitrile,



b. p. 245—247° or 131—133°/14 mm.; $[\alpha]_D^{25} + 3.2^\circ$. On hydrolysis with sulphuric acid, the nitrile gives the original amide, and on reduction with sodium and absolute alcohol readily gives dimethylcampholylamine, $\text{CHMe}_2\cdot\text{C}_8\text{H}_{13}\cdot\text{CH}_2\cdot\text{NH}_2$, b. p. 123—124°/20 mm.; $[\alpha]_D^{25} + 30.1^\circ$, which is very basic and gives a sulphate, a hydrochloride, and a platinichloride.

Dimethylcampholyl chloride reacts with absolute alcohol, giving ethyl dimethylcampholate, b. p. 138°/24 mm.; $[\alpha]_D^{25} + 37.2^\circ$; and with sodium phenoxide, giving phenyl dimethylcampholate, b. p. 190—195°/30 mm., as the latter ester on reduction with sodium and absolute alcohol yields dimethylcampholyl alcohol,



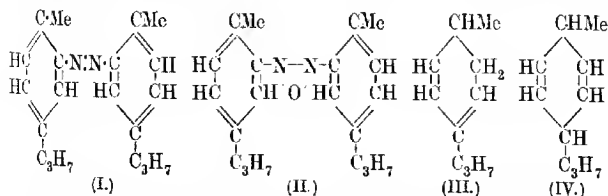
b. p. 139—140°/20 mm.; $[\alpha]_D^{25} + 32^\circ$.

W. G.

A New Method for the Resolution of Asymmetric Compounds. AKIRA SHINOMURA and JULIUS BEREND COHEN (T., 1921, 119, 1816—1825).

Chenopodium Oil. THOMAS ANDERSON HENRY and HUMPHREY PAGET (T., 1921, 119, 1714—1724).

The Essential Oil of *Mosla japonica*, Maxim. YOSHIATSU MURAYAMA (*J. Pharm. Soc. Japan*, 1921, 769—786; cf. Haneda, *ibid.*, 1889, No. 92; Shimoyama, A., 1893, ii, 181; Hoshino, *J. Chem. Ind., Japan*, 1919, 22, 557).—The essential oil of *Mosla japonica*, Maxim, freed from *p*-cymene, was separated by repeated fractional distillation into a terpene fraction, b. p. 173—175°, or 59—60°/10 mm., and a sesquiterpene fraction, b. p. 125—128°/10 mm. From the former, a new terpene, $C_{10}H_{16}$, *moslene*, was isolated, which resembles, but is not identical with, the crithmene of Francesconi and Sernagiotto (A., 1913, i, 636). By passing hydrogen chloride into a cooled ethereal solution of the terpene, it yields a *hydrochloride*, $C_{10}H_{16} \cdot 2HCl$, m. p. 51°; this suggests the presence of α -terpinene and the formation of $C_{10}H_{16}(OH)_2$, m. p. 235—238°, by oxidation with potassium permanganate, indicates the presence of γ -terpinene. The terpene yields a *nitrosochloride*, $C_{10}H_{15}ONCl$, white crystals, m. p. 111°, which by treatment with piperidine in alcoholic solution is converted into the *nitrolpiperidide*, lustrous, small plates, m. p. 142—143°, and by heating with aniline, into the *nitrolanilide*, small prisms, m. p. 126—128°. *Moslene nitrosate*, forming needles, m. p. 114°, is obtained by adding a mixture of glacial acetic acid and nitric acid (*d* 1.4) to a cooled mixture of the terpene, amyl nitrite, and glacial acetic acid. By warming the nitrosochloride with sodium ethoxide, an *azoxy*-compound, m. p. 52—53°, and an *azo*-compound, orange-yellow crystals, m. p. 85—87°, are formed. On reduction with zinc dust and glacial acetic acid, the *azo*- or *azoxy*-compound gave white crystals, of the composition $C_{20}H_{34}(NH_2)_2 \cdot 2HCl$, which changes its colour at about 262° and decomposes at 280—292°; this gives, with chloroauric acid, a blood-red coloration and then a greyish precipitate. The platinumchloride forms yellow grains, and does not melt below 300°. By warming 2-nitro-*p*-cymene (*Skimmels Bericht*, 1919, 130) with zinc dust in sodium ethoxide solution on a water-bath, an *azo*-compound is produced which is identical with that obtained from moslene nitrosochloride. The constitution of the *azo*-compound therefore corresponds with (I) and that of the *azoxy*-compound with (II); it follows that the new terpene, moslene, is a dihydro-*p*-cymene. There are theoretically five isomeric dihydro-*p*-cymenes, three of which are known. Moslene must therefore have the constitution (III) or (IV).



From the sesquiterpene fraction, caryophyllene was obtained and identified by the formation of its *nitrosochloride*, m. p. 161° (the *k k 2*

thoroughly purified nitrosochloride melts at 177°), nitrosate, m. p. $147-148^{\circ}$, and alcohol, m. p. $82-84^{\circ}$.
K. K.

Occurrence of Moslene in Essential Oils containing *p*-Cymene. YOSHIATSU MURAYAMA (*J. Pharm. Soc. Japan*, 1921, No. 475, 786-790).—As the author has isolated a new terpene, moslene, from the essential oil of *Mosla japonica*, Maxim (cf. preceding abstract), its presence was sought for in other essential oils containing *p*-cymene, and was proved in the terpene fractions of ajowan oil (from the fruits of *Ptychotis Ajowan*) and the oil of *Mosla grosseserrata*, Maxim (cf. Murayama, A., 1920, i, 624) by the formation of the nitrosochloride, nitrosopiperidide, and nitrosate respectively.
K. K.

The Solubility of some New Resins. P. NICOLARDOT and CH. COFFIGNIER (*Bull. Soc. chim.*, 1921, [iv], 29, 917-921).—The solubilities of the resins from *Hopea ricopei*, and *Aucoumea Klaineana*, and of Dammar Cambodge, and light red Dammar (*Thorea vulgaris*) resins in ethyl, methyl, and amyl alcohols, ether, chloroform, benzene, acetone, turpentine, carbon tetrachloride, benzaldehyde, aniline, and amyl acetate are given.
W. G.

The Solubility of some Resins from Cochin-China. P. NICOLARDOT and CH. COFFIGNIER (*Bull. Soc. chim.*, 1921, [iv], 29, 921-932).—Using the same solvents (cf. preceding abstract), the authors have determined the solubilities of the resins of *Hopea odorata*, *Hopea dealbata*, *Shorea vulgaris*, *Shorea hypochra*, *Thorea thorelli*, *Hopea pierrei*, *Anisoptera*, *Natica astrotica*, and the resin from the Chinese pine.
W. G.

The Relative Activity of Various Allotropic Forms of Sulphur towards Caoutchouc. D. F. TWISS and F. THOMAS (*J. Soc. Chem. Ind.*, 1921, 40, 48-50r).—Mixtures of plantation rubber with ordinary powdered sulphur and with insoluble sulphur respectively, with the additional presence of 1% of aldehyde-ammonia as catalyst, were vulcanised at 98° , 108° , and 118° . A mixture of synthetic rubber with sulphur was vulcanised at 168° , 178° , and 188° . From the relative rate of vulcanisation in the first set of experiments and the temperature coefficient of the chemical reaction in the second set, the conclusion is drawn that although S_{μ} , as a vulcanising agent, is a little less active than S_{α} or S_{π} , the difference is surprisingly small.
D. F. T.

The Discontinuity of Vulcanisation in the Presence of Organic Accelerators. D. F. TWISS (*J. Soc. Chem. Ind.*, 1921, 40, 242-248r).—When a mixture of natural caoutchouc (90) and sulphur (10) is heated with the additional presence of zinc oxide (1) and hexamethylenetetramine (0.5-2.5), the course of the vulcanisation process, as indicated by the gradual physical alteration in the caoutchouc, is not continuous (see Twiss and Howson, A., 1920,

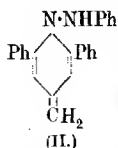
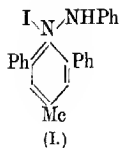
i, 751). The temporary softening effect which succeeds the initial period of normal alteration is probably due to a "depolymerising" effect by the hexamethylenetetramine. By reducing the proportion of sulphur in the mixture, it is possible to accentuate this effect and render it more persistent. This effect of hexamethylenetetramine is also observable in the absence of zinc oxide, a higher proportion of combined sulphur than the normal being necessary to produce a condition of over-vulcanisation. Indications of a similar phenomenon are given in a milder degree by many other vulcanisation catalysts. In the presence of more zinc oxide the positive effect of such catalysts is increased and the inverse effect is less evident. On the other hand, the activity of other catalysts is but little influenced by zinc oxide; a glycerol solution of potassium hydroxide, for instance, is scarcely affected by the presence of zinc oxide or by previous saturation with hydrogen sulphide.

D. F. T.

Saponins. IV. The Saponins of the Nuts of *Pseudo-phoenix Vinifera*, Beccari, and their Magnesium and Calcium Salts. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1921, 40, 542—552; cf. A., 1917, i, 41, 70).—These saponins belong to the group which is precipitated neither by normal nor by basic lead acetate, but by the basic acetate in presence of ammonia. They exist partly free and partly as compounds of calcium and magnesium. Their complete hydrolysis is a matter of some difficulty; the resulting saccharides are rhamnose, levulose, and *d*-galactose. Pentoses, fucose, dextrose, *d*-mannose, and acids of the glycuronic group are absent. Sapogenins produced by hydrolysis constitute about 40% of the saponin and consist of a mixture of crystalline and amorphous substances. Two have been isolated in crystalline form, m. p. 328° and 215—216° respectively. The formula of the latter is $C_{29}H_{32}O$, and the substance is of the nature of phytosterol. The author considers that sapogenins are allied to the terpenes and that a more extended study of the crystalline sapogenins should be made on a larger scale.

H. J. E.

2:6-Diaryl-4-methylpyrylium Salts and Pyranhydrones. WILHELM SCHNEIDER and FRITZ SEEBACH (*Ber.*, 1921, 54, [B], 2285—2298).—In continuation of previous work (Schneider and Meyer, this vol., i, 680), it has now been found possible to isolate the pyrylium salts from the products of the reaction directly in the form of their sulphaacetates, thereby effecting a considerable improvement in the yields in certain cases. From aqueous solutions of the salts, it is possible by cautious addition of sodium hydroxide to precipitate the *v*-bases, but these pass into pyranhydrones when desiccated. The latter are, however, more conveniently obtained by the addition of concentrated sodium acetate solution to the sulphaacetates dissolved in water. Attempts to obtain the pyranhydrones in the crystalline condition have not yet been successful. The replacement of sodium acetate by weak organic bases, for example, aniline, phenylhydrazine, for the decomposition of

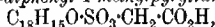


pyrylium salts leads unexpectedly to the production of pyridine derivatives. Thus, 2:6-diphenyl-4-methylpyrylium iodide and phenylhydrazine give 1-anilino-2:6-diphenyl-4-methylpyridinium iodide (I), which is converted by alkali into the anhydro-base (II). The latter class of substance

has only been obtained up to the present from 4-methyl compounds.

The requisite sulphaetic acid is prepared by cautious admixture of acetic anhydride (100 c.c.) and concentrated sulphuric acid (30 c.c.) and subsequent gentle heating of the mixture during two to three hours at a temperature which does not exceed 80°; at the end of this time free sulphuric acid is present only in traces.

Acetophenone is slowly converted by the mixture just described at 45—50° into 2:6-diphenyl-4-methylpyrylium sulphaacetate,



slender, yellow needles, m. p. 204°, from which the corresponding chloride, bromide, pale yellow needles, m. p. 194°, and iodide, long, red needles, m. p. 222°, are obtained; the latter salt is remarkable in that its solutions in dilute acid are pale yellow in colour and when cooled deposit the red salt without any previous darkening in shade. In a similar manner, but with a mixture containing a smaller proportion of sulphuric acid, anisole yields 2:6-di-p-anisyl-4-methylpyrylium sulphaacetate, $\text{C}_{20}\text{H}_{19}\text{O}_3\cdot\text{SO}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, matt yellow needles, m. p. 198°. The corresponding chloride, $\text{C}_{20}\text{H}_{19}\text{O}_3\text{Cl}$, separates from alcoholic solution on the addition of ether as an orange-yellow, crystalline powder, m. p. 173°, from a mixture of alcohol and benzene in coarse, flesh-red needles ($+\text{C}_6\text{H}_6$) and slender, pale yellow needles ($+\frac{1}{2}\text{C}_6\text{H}_6$). The bromide forms slender, orange-yellow crystals, m. p. 193°, whereas the iodide is composed of slender, yellow needles or brown crystals, m. p. 204°. In this instance, the use of the sulphaacetate for the preparation of the corresponding pyranhydrone (cf. Schneider and Meyer, *loc. cit.*) is particularly advantageous.

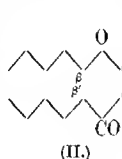
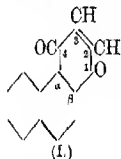
1-Anilino-2:6-diphenyl-4-methylpyridinium iodide, a yellow, crystalline powder, m. p. 200°, is prepared by the addition of a solution of phenylhydrazine in benzene to a suspension of 2:6-diphenyl-4-methylpyrylium iodide in the boiling solvent. It is converted by a slight excess of very dilute aqueous sodium or potassium hydroxide solution into the anhydro-base (formula II above) dark blue needles, or hexagonal leaflets, m. p. 108°; it is somewhat unstable in solution in organic media. It is practically insoluble in water, in contact with which it behaves as a strong base which is able to displace ammonia from its salts. It readily re-forms the yellow quaternary pyridinium salts with acids and combines even with very weak acids, for example, carbonic. 2:4:6-Triphenylpyrylium iodide, a red, crystalline powder, m. p. 222°, is converted by phenylhydrazine in the presence of boiling benzene into the almost colourless 1-anilino-2:4:6-triphenylpyridinium

iodide, which does not give a coloured anhydro-base when heated in aqueous-alcoholic solution with dilute alkali hydroxide. H. W.

Production of Coumarins from Maleic and Malic Acids.

G. C. BAILEY and F. BOETTNER (*J. Ind. Eng. Chem.*, 1921, **13**, 905—906).—By heating together phenol and maleic acid in the presence of various dehydrating agents coumarin was not produced and with malic acid no appreciable quantities were formed. *m*-Cresol and malic acid in the presence of sulphuric acid produced methylcoumarin, a 50% yield on the weight of malic acid being obtained with a very pure *m*-cresol, and a 38—40% yield with an 80% *m*-cresol. Methylcoumarin is only one-tenth as toxic to white mice as coumarin. The perfume value of methylcoumarin is claimed to be equal to that of coumarin and its taste similar to, but slightly less intense than, that of the natural product. S. S. A.

Sulphoacetic Acid as Condensing Agent. III. Acetyl-naphthyl Methyl Ether and 3-Acetyl-2-methyl- β -naphthachromone- α . WILHELM SCHNEIDER and FRITZ KUNAU (*Ber.*, 1921, **54**, [B], 2302—2310; cf. Schneider and Sechach, this vol., i, 877). α -Naphthyl methyl ether is transformed by an acetylating mixture prepared from acetic anhydride (70 c.c.) and concentrated sulphuric acid (10 c.c.) into 4-methoxy- α -naphthyl methyl ketone which has been obtained previously by Gattermann from α -naphthyl methyl ether, aluminium chloride, and acetyl chloride. Under similar conditions, β -naphthyl methyl ether is converted partly into 2-methoxy- α -naphthyl methyl ketone (cf. Fries, this vol., i, 424) (it is interesting to note that the Gattermann synthesis gives the isomeric 2-methoxy- β -naphthyl methyl ketone) and 3-acetyl-2-methyl- β -naphthachromone- α . The formation of the latter from 2-methoxy- α -naphthyl methyl ketone depends obviously on primary acetylation of the methoxy-group by the sulphoacetic acid,



internal condensation of 1-acetyl- β -naphthyl acetate with loss of water, and formation of the pyrone ring, and subsequent acetylation of the 2-methyl- β -naphthachromone- α in position 3.

It is proposed to term the isomeric β -naphthachromones (annexed formulæ, I and II), β -naphthachromone- α , and β -naphthachromone- β' respectively.

4-Methoxy- α -naphthyl methyl ketone crystallises in pale yellow, irregular leaflets, m. p. 70—71° (*oxime*, colourless leaflets, m. p. indefinite, 122—127°, *picrate*, slender, red needles, m. p. 119—121°). The pyrylium derivative does not appear to be formed from α -naphthyl methyl ether and sulphoacetic acid. β -Naphthyl methyl ether likewise does not yield a pyrylium derivative, but is transformed into 2-methoxy- α -naphthyl methyl ketone, colourless needles, m. p. 56—57°, and 3-acetyl-2-methyl- β -naphthachromone- α , long, coarse, pale yellow needles, m. p. 157—158°. The latter is converted by hydroxylamine hydrochloride in boiling absolute

alcoholic solution in the presence of barium carbonate into a *substance*, pale brown needles, m. p. 250° (decomp.) (the amount was too small to allow of further investigation), the *dioxime*, $C_{18}H_{12}O(N\cdot OH)_2$, colourless needles, m. p. 201°, and *monoxime*, yellowish-white, irregular leaflets, m. p. 153°. 3-Acetyl-2-methyl- β -naphthachromone- α gives unstable additive *products* with bromine [m. p. 105–110° (decomp.)] and hydrogen chloride. It is converted by alcoholic ammonia into 2-methyl- β -naphthachromone- α , pale yellow, irregular leaflets, m. p. 168°. The latter gives an unstable additive *compound*, m. p. 100° (decomp.), with bromine, an *oxime*, slender needles, m. p. 182°, and an *additive compound*, $C_{18}H_{12}O_2N$, yellow needles, m. p. 137°, with ammonia. 3-Acetyl-2-methyl- β -naphthachromone- α is converted by boiling dilute aqueous sodium hydroxide solution into β -naphthol and 2-hydroxy- α -naphthyl methyl ketone, m. p. 64° (cf. Fries, *loc. cit.*). H. W.

Derivatives of 3-Oxy(1)thionaphthen. SAMUEL SMILES and ERNEST WILSON McCLELLAND (T., 1921, 119, 1810–1816).

Carnitine. R. ENGELAND (*Ber.*, 1921, 54, [B], 2208–2213).—Carnitine (A., 1905, i, 726; 1907, i, 264; 1908, i, 41, 842; 1909, i, 557) has been regarded by Fischer and Göddertz (A., 1911, i, 19) as identical with the hydroxybutyrobetaine, $O\langle \begin{smallmatrix} NMe_3-CH_2 \\ CO-CH(OH) \end{smallmatrix} \rangle CH_2$, but this view of its constitution is not readily reconcilable with the observation that it easily loses water when treated with concentrated sulphuric acid at about 130° (or by treatment with red phosphorus and concentrated hydriodic acid at 150–160°, or even at the boiling point of the mixture under atmospheric pressure) and yields *apocarnitine*. The compound prepared by Fischer and Göddertz, on the other hand, remains unchanged under these conditions and the non-identity of the two substances is further confirmed by the observation that *carnitine aurichloride* has m. p. 150–151° after softening at 145°, whereas the aurichloride of Fischer's compound melts at 166–171° (according to the rate of heating) after softening at 160–161°. Carnitine is more probably represented by the formula $O\langle \begin{smallmatrix} NMe_3-CH_2 \\ CO-CH-CH_2-OH \end{smallmatrix} \rangle$ and its

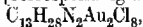
oxidation to β -homobetaine is explained by the instability of the intermediately formed "trimethylaminomethylmalonic acid," since it is found that positively-substituted malonic acids readily lose carbon dioxide even when heated in aqueous solution. The catalytic hydrogenation of *apocarnitine* to the corresponding saturated betaine can only be accomplished with some difficulty and uncertainty; the product formed (aurichloride, m. p. 172–173°) resembles most closely γ -butyrobetaine, but the identity of the two substances is not established with certainty, and, at present, it can only be stated that it differs decidedly from α -n- and α -iso-butyrobetaine and from β -isobutyrobetaine.

apoCarnitine aurichloride, $C_{17}H_{14}O_2N, AuCl_4$, crystallises in pale yellow, lustrous leaflets, m. p. 190–195° (decomp.), after softening

at about 180° ; the corresponding *chloride* forms long, hygroscopic needles. Carnitine chloride is converted by concentrated sulphuric acid at 90 — 100° into carnitine ether, which was isolated in the form of its *aurichloride*, $C_{11}H_{30}O_5N_2 \cdot 2AuCl_4$, m. p. (indefinite) 175 — 182° . H. W.

Hygrine Alkaloids. IV. Di-1-methyl-2-pyrrolidylmethane. KURT HESS and FRANZ ANSELM (*Ber.*, 1921, **54**, [B], 2310—2326; cf. A., 1920, i, 497).—It has been shown previously that cuskhygrine is a derivative of di-1-methyl-2-pyrrolidylmethane; attempts to synthesise the latter are now recorded. This can be effected by the catalytic reduction of di-2-pyrrolyl ketone by hydrogen in the presence of platinum to di-2-pyrrolidylmethane (the course of the reaction is unusual and due to the presence of the carbonyl group, since the corresponding methylene compound is not reducible under these conditions) and methylation of the latter. The base is not homogeneous and can be separated into at least two biquaternary methylammonium iodides. Further examination of the base from cuskhygrine has disclosed the fact that it also is not uniform, and can be transformed into two well-defined biquaternary methylammonium iodides which are not identical with those obtained from the synthetic compound. The existence of these optically inactive isomerides appears to be explicable only on the assumption that the nitrogen atoms function as asymmetric centres and that di-1-methyl-2-pyrrolidylmethane resembles stereochemically the saccharic acids and exists in six optically inactive forms, two of which belong to the non-resolvable meso-type. In favour of this conception, the isolation of a possible fifth isomeride is recorded.

Di-2-pyrrolyl ketone, m. p. 156 — 157° , is conveniently prepared by passing a current of carbonyl chloride into an ethereal solution of magnesium pyrrolyl bromide. It gives a *hydrazone*, m. p. 115 — 117° , which is converted by sodium ethoxide at 150° into di-2-pyrrolylmethane, b. p. 163 — $167^{\circ}/12$ mm., m. p. 73° [Pictet and Rilliet (A., 1907, i, 445) give m. p. 66°]. The ketone is reduced by hydrogen in the presence of platinum (the apparatus is fully described and depicted in the original) to a mixture of di-2-pyrrolidylmethanes, b. p. 112 — $122^{\circ}/15$ mm., which is converted by formaldehyde and formic acid into a mixture of di-1-methyl-2-pyrrolidylmethanes, b. p. 115 — $120^{\circ}/15$ mm. The latter, when treated with methyl iodide, gives two crystalline *biquaternary methiodides*, needles, m. p. 180° , and four-sided platelets, m. p. 290° (incipient decomp.) [corresponding *aurichloride*,



yellow, microcrystalline precipitate, m. p. about 275° (decomp)], whilst apparently a third *isomeride*, cubes or prisms, m. p. 146 — 147° , was isolated in quantity too small to permit of analysis. The base from cuskhygrine is similarly convertible into two biquaternary methiodides, m. p. 263° and 201° respectively, the latter of which has been described previously by Hess and Fink (A., 1920, i, 497).

The action of hydrazine hydrate on cuskhygrine (Hess and Fink, *loc. cit.*) has been further investigated, and it is now found that in the presence of a little water cuskhygrine- α -hydrazone, b. p. 182—185°/11 mm., and relatively much smaller amounts of *hygrine hydrazone*, b. p. 125—130°/11 mm., are produced. The latter is hydrolysed readily by dilute sulphuric acid to hygrine, and is converted by sodium ethoxide solution at 150° into α -1-methyl-2-pyrrolidylpropane, b. p. 140—142° (cf. A., 1914, i, 199). The isomerism of the cuskhygrine- α - and - β -hydrazones remains unexplained, but it is shown that the former regenerates cuskhygrine smoothly under the influence of acids.

The transformation of cuskhygrine into hygrine by alkalis has been recorded previously; the change can also be produced by hydrochloric acid at 170—180°.

Attempts to oxidise 1-methyl-2-pyrroldylacetic acid to 1-methyl-pyrroldine-2-carboxylic acid were unsuccessful by reason of the unexpected stability of the original material.

H. W.

Constitution of Matrine. I. HEIZABURŌ KONDŌ and SHIN-ICHI SATŌ (*J. Pharm. Soc. Japan*, 1921, 659—679).—*Matrine*, $C_{15}H_{21}ON_2$, is one of the principal alkaloids of the roots of *Sophora flavescens*, Ait. (*S. angustifolia*, S. and Z.) and is a monoacidic tertiary amine. Of the two nitrogen atoms, one forms a lactam ring with a carboxyl group and is changed to an imino-group by hydrolysis with alkali, *matrinic acid* being formed (*ibid.*, 1889, No. 84; 1903, Nos. 260—262). *Matrine hydrochloride* was mixed thoroughly with fourteen times its weight of zinc dust and distilled in a combustion tube, the distillate being absorbed in dilute hydrochloric acid. The distillate was made alkaline, and subjected to steam distillation. The residue consisted mainly of *matrinic acid* mixed with a black resin; the colourless oil of peculiar odour which distilled was acidified with hydrochloric acid and precipitated with mercuric chloride, the mercury was removed by means of hydrogen sulphide, and the two admixed bases were separated by distillation under reduced pressure.

The base, $C_{10}H_6N$, distilled at 87°/19 mm. or 188—189°/760 mm., and gave the following derivatives: *hydrochloride*, deliquescent, long needles; *mercurichloride*, white prisms, m. p. 206°; *picrate*, yellow prisms, m. p. 165°; *aureichloride*, yellow lamellæ, m. p. 143—144°; *platinichloride*, long lamellæ, decomposing at 216—217°; *methiodide*, m. p. 241°. From the methiodide the corresponding *ammonium chloride* was prepared as deliquescent, colourless needles; this gave a *mercurichloride*, m. p. 216°; *picrate*, yellow needles, m. p. 211°; *platinichloride*, octahedra, m. p. 223—224° (decomp.); and *aureichloride*, yellow needles, m. p. 239—240°. The *methylammonium hydroxide* of the base, a brown syrup, shows the characteristic behaviour of a base of this class, and on distillation with potassium hydroxide yields methyl alcohol, the original base, and some products of decomposition.

The second base, *matridine*, $C_{15}H_{26}N_2$, white needles, m. p. 76°, does not distil at 160°/19 mm., and is a reduction product of *matrine*,

the carboxyl group having been changed into the CH_2 -group. Its properties resemble those of matrine, but it does not yield matrinic acid when hydrolysed. The hydrochloride, $\text{C}_{15}\text{H}_{26}\text{N}_2 \cdot 2\text{HCl}$, long, white needles, sublimes without melting; the aurichloride, forms yellow lamellæ, m. p. 216° . K. K.

Strychnos Alkaloids. XXIX. Oxidation of Cryptobrucinolone and its Preparation from Brucinolone-b. HERMANN LEUCHS, EMIL HELLRIGEL, and HARRY HEERING (*Ber.*, 1921, 54, [B], 2177—2190).—The crude mixture of *a*- and *b*-acetylbrucinolone is converted by methyl alcoholic ammonia at 100° into the pure *b*-form; attempts to effect this transformation more conveniently by the use of ethyl-alcoholic potassium hydroxide solution resulted in the preparation of a mixture of ethoxydihydrobrucinolone and cryptobrucinolone (Leuchs and Pierce, A., 1912, i, 898), thus giving a convenient method of obtaining the latter which has now been subjected to prolonged examination. It is remarkable that in the series: brucinolone-*a* $\xrightarrow[\text{cold alkali}]{\text{NH}_3}$

brucinolone-*b* $\xrightarrow[\text{alkali}]{\text{hot alcoholic}}$ cryptobrucinolone, a double bond

appears first to be displaced further from the nitrogen atom by one carbon atom and then, under similar conditions, to resume its previous position; thus probably indicating further changes in the remainder of the molecule under the influence of alcoholic potassium hydroxide solution. The change does not, however, appear to affect the aromatic residuc of the brucine molecule, since it has the same reactions in cryptobrucinolone as in the other brucinolones.

Ethoxydihydrobrucinolone, $\text{C}_{23}\text{H}_{28}\text{O}_6\text{N}_2$, colourless, lustrous prisms (+1MeOH), m. p. generally about 110° , but occasionally about 132° after softening at 106° , $[\alpha]_D^{25} -44.2^\circ$ in glacial acetic acid solution; pointed prisms (+1EtOH), m. p. 135° (decomp.) after softening at 130° ; anhydrous, m. p. $105-125^\circ$, $[\alpha]_D^{25} -44.0^\circ$, and cryptobrucinolone, pale greenish-yellow leaflets, m. p. $190-192^\circ$, $[\alpha]_D^{25} -150.9^\circ$ when dissolved in glacial acetic acid, are prepared by the action of hot alcoholic potassium hydroxide solution on pure or crude acetylbrucinolone-*b*; in addition, there is isolated a substance which is soluble in alkali hydroxide and is termed *ethoxydihydrobrucinolone-III*, $\text{C}_{21}\text{H}_{24}\text{O}_6\text{N}_2$, colourless leaflets or slender needles, m. p. $219-221^\circ$ after softening at 213° , $[\alpha]_D^{25} -49.5^\circ$ in glacial acetic acid solution. The ethoxydihydro-compound is converted by alcoholic potassium hydroxide solution into cryptobrucinolone, whereas the latter is unaffected. *Ethoxydihydrobrucinolone acetate* forms colourless prisms, m. p. $219-220^\circ$, $[\alpha]_D^{25} -78.2^\circ$ in glacial acetic acid solution. Cryptobrucinolone is converted by 5*N*-nitric acid at 0° into the corresponding *quinone*, $\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_2$, lustrous, red needles, which become discoloured above 250° ; the latter is reduced by sulphurous acid to the *quinol*, $\text{C}_{16}\text{H}_{18}\text{O}_6\text{N}_2$, which is amorphous. Similarly, 14*N*-nitric acid at 0° transforms cryptobrucinolone into the *nitroquinone*, $\text{C}_{16}\text{H}_{16}\text{O}_7\text{N}_3$, orange-coloured needles, which is reduced to the *nitroquinol*,
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$C_{19}H_{17}O_7N_3$, ochre-yellow, rectangular prisms, decomp. $263-265^\circ$. *Acetylcryptobrucinolone*, short, prismatic rods, m. p. $272-274^\circ$, $[\alpha]_D^{25} -199.5^\circ$ in glacial acetic acid solution, is prepared with the aid of sodium acetate and acetic anhydride; it is oxidised by potassium permanganate in acetone solution to an acid, $C_{23}H_{24}O_{10}N_2 \cdot 0.5H_2O$, slender, colourless needles, m. p. about 280° (slight decomp.), which is most definitely characterised by its copper salt, $C_{23}H_{23}O_{10}N_2Cu \cdot 8H_2O$, apple-green needles and prisms and ferric salt, $(C_{23}H_{23}O_{10}N_2)_2Fe \cdot OH$, brownish-violet prisms or needles. The acid is decomposed by 12*N*-hydrochloric acid at 100° into oxalic and acetic acids and non-crystalline basic products; it must therefore contain the groups $:N \cdot CO \cdot CO_2H$ and $CO_2H \cdot Cl$ formed from the arrangement $:N \cdot CO \cdot CH \cdot CH \cdot Cl$. Cryptobrucinolone is oxidised by permanganate in acetone solution to a substance crystallising in slender needles, m. p. 260° (decomp.) after softening at 230° , which dissolves in a large excess of alkali hydroxide solution.

Acetoxydihydrobrucinolone-I forms short, thick prisms, m. p. $253-254^\circ$, $[\alpha]_D^{25} -22.3^\circ$ in glacial acetic acid solution. When cryptobrucinolone is heated with acetic anhydride at 100° (in the absence of sodium acetate) it is converted into a mixture of the corresponding acetate and dehydrobrucinolone acetate [brucinolone acetate-*c*], yellow needles or prisms, m. p. 312° , $[\alpha]_D^{25} -431^\circ$ in glacial acetic acid solution, which is identical with the product obtained by the oxidation of acetylbrucinolone-*b* in acetone solution (A., 1912, i, 210). When heated with methyl-alcoholic ammonia at 100° it gives (?) *dehydrobrucinolone*, yellow, rectangular platelets, m. p. about 315° (decomp.), $[\alpha]_D^{25} -376^\circ$ in glacial acetic acid solution, from which the acetate is readily re-formed. Brucinolone-*b* appears to be partly converted by acetic anhydride at 100° into dehydrobrucinolone acetate. H. W.

Acid Methylarsenate of Strychnine. J. BOUILLLOT (*J. Pharm. Chim.*, 1921, [vii], 24, 289-294).—Conflicting statements have appeared at various times regarding the composition and properties of strychnine methylarsenate, but it is now definitely shown that the strychnine methylarsenate of commerce is actually the acid salt of the composition $AsMeO(OH)_2 \cdot C_{21}H_{22}O_2N_2 \cdot 2H_2O$. This salt is prepared by dissolving in hot aqueous alcohol equimolecular proportions of methyarsenic acid and strychnine, and allowing to crystallise by spontaneous evaporation, preferably in presence of sulphuric acid in a vacuum. Colourless needles are thus obtained, soluble in 14.5 parts of water at 20° , and in 146 parts of 90% alcohol. In 5% aqueous solution $\alpha_D -21^\circ$. The salt is stable at ordinary temperatures, but commences to decompose at temperatures above 60° . G. F. M.

Phenacyl- and Dihydroxyphenacyl-derivatives of Theobromine and Theophylline, and their corresponding Secondary Alcohols. C. MANNICH and S. KROLL (*Ber. deut. Pharm. Ges.*, 1921, 31, 291-310).—With the object of preparing new

caffeine derivatives in which the stimulating action of caffeine on the nerve system was eliminated whilst the cardiac action was retained, substances were prepared in which the phenacyl radicle, $\text{COPh}\cdot\text{CH}_2-$, and the group, $\text{C}_6\text{H}_5(\text{OH})_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2-$, characteristic of adrenaline, were introduced into the xanthine molecule. The desired physiological result was not obtained, however, phenacyltheobromine and phenacyltheophylline showing no advantage over theophylline, and the adrenaline-caffeine derivatives being physiologically inactive. The preparation and properties of the following are described: 7-Phenacyltheophylline, $\begin{array}{c} \text{NMe}\cdot\text{CO}\cdot\text{C}=\text{N}\cdot\text{CH}_2\cdot\text{COPh}, \\ \text{CO}\cdot\text{NMe}\cdot\text{C}\cdot\text{N}\cdot\text{CH} \end{array}$

prepared by the action of *m*-bromoacetophenone on sodium theophylline, forms white, silky needles, m. p. 188°. It yields an *oxime*, m. p. 233°, and a *semicarbazone*, m. p. 225°. When reduced with palladium and hydrogen, it gives the corresponding secondary alcohol, α -3:4-dimethoxyphenyl- β -theophyllinoethanol, $\text{C}_5\text{H}_4\text{HO}_2\text{Me}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$, m. p. 159°.

3:4-Dimethoxy-7-phenacyltheophylline, prepared by condensing sodium theophylline with *m*-bromoacetoveratrone, forms white needles, m. p. 212°, and gives an *oxime*, m. p. 216°. On reduction with palladium and hydrogen, it gives the corresponding secondary alcohol, α -3:4-dimethoxyphenyl- β -theophyllinoethanol, m. p. 181°. On attempting to demethylate this with hydriodic acid decomposition ensued.

3:4-Dihydroxyphenacyltheophylline was obtained by demethylating the above compound with hydriodic acid; it gives a green coloration with ferric chloride, turning to red with ammonia (catechol reaction). Its *diacetyl* derivative melts at 203°. On reduction with palladium and hydrogen followed by hydrolysis it is converted into the corresponding secondary alcohol, α -3:4-dihydroxyphenyl- β -theophyllinoethanol, which may be regarded as a derivative of adrenaline on the one hand and of caffeine on the other. The substance forms a grey, crystalline powder, which decomposes towards 220° without melting. Its *triacetyl* derivative forms white needles, m. p. 114°. 1-Phenacyltheobromine, prepared similarly to the corresponding theophylline derivative, melts at 171°, and gives an *oxime*, m. p. 215°, and a *semicarbazone*, m. p. 215–216°. The corresponding secondary alcohol, α -phenyl- β -theobrominoethanol, forms white needles, m. p. 110°, with loss of 1 mol. of water of crystallisation. The anhydrous substance then melts at 147°.

3:4-Dimethoxyphenacyltheobromine, prepared in similar manner to the theophylline derivative, forms silky crystals, m. p. 227°, and gives the corresponding secondary alcohol, m. p. 195°, on reduction with aluminium amalgam in dilute alcoholic solution. Demethylation with hydriodic acid of the methoxyphenacyltheobromine gave grey needles of 3:4-dihydroxyphenacyltheobromine, decomposing at 280° without melting. Its *diacetyl* derivative, m. p. 208°, on reduction with aluminium amalgam in alcoholic solution, followed by hydrolysis with alcoholic potassium hydroxide in absence of air, gives α -3:4-dihydroxyphenyl- β -theobrominoethanol,

forming a grey, crystalline powder decomposing at 170° without melting. It gives a white, crystalline *triacetate*, m. p. 147° .

G. F. M.

***d*-Lupanine, $C_{15}H_{24}ON_2$.** GÖSTA MOLANDER (*Ber. deut. Pharm. Ges.*, 1921, **31**, 265—270).—Contrary to the statements of Beckel (A., 1911, i, 743; 1913, i, 86), the action of alcoholic bromine on lupanine hydrochloride does not result in a decomposition into two new bases, but gives a brominated compound of the composition $C_{15}H_{24}ON_2 \cdot HBr \cdot Br_2$ or $C_{15}H_{22}Br_2ON_2 \cdot HBr$ in yellow crystals, from which bromine is readily eliminated by boiling with alcohol, with the formation of colourless crystals of lupanine hydrobromide, m. p. 240° . *d*-Lupanine is very resistant also to the action of fuming hydrochloric acid under pressure, and to 50% potassium hydroxide. It yields a syrupy base having a crystalline hydrochloride, m. p. 158° , when boiled with 40% alcoholic potassium hydroxide.

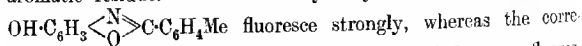
G. F. M.

Crystallographic Descriptions of some Pyridine and Picoline Derivatives. MARY WINEARLS PORTER (T., 1921, **119**, 1769—1773).

Derivatives of Tetrahydrocarbazole. WILLIAM HENRY PERKIN, JUN., and SYDNEY GLENN PRESTON PLANT (T., 1921, **119**, 1825—1839).

Relation between Fluorescence and Chemical Constitution in Benzoxazole Derivatives. F. HENRICH (*Ber.*, 1921, **54**, [B], 2492—2511).—The author has shown that 5-hydroxy-1-phenyl-3-methylbenzoxazole exhibits green fluorescence in various solvents even after purification by repeated crystallisation (A., 1897, i, 446; 1899, i, 171). This compound and other benzoxazole derivatives have recently been prepared by Skraup (A., 1919, i, 598), who states that they lose their fluorescent properties when repeatedly purified by crystallisation from solutions treated with animal charcoal. The author has again prepared this compound and subjected it to repeated fractional crystallisation, treatment with animal charcoal, dissolution in alkali hydroxide solution, and reprecipitation, etc., the fluorescence remaining undiminished.

A number of oxazole derivatives have been prepared and examined to ascertain which of them exhibit to the unassisted eye fluorescence in solution. A distinction must be drawn between fluorescence shown in aqueous alkali solution and organic solvents, especially alcohol, and that shown in concentrated sulphuric acid solutions, which fluoresce the most readily. In order to convert benzoxazole into substitution products fluorescing visibly in solution, the first essential is for the μ -[1]-position to be occupied by an aromatic residue. The three 5-hydroxy-derivatives of the form

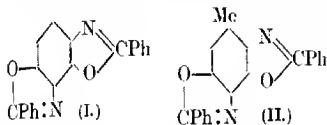


sponding compound with benzyl in place of tolyl shows no fluorescence even if the 3-position is occupied by a methyl group. The presence in position 5 of a salt-forming group, preferably hydroxyl,

intensifies the fluorescent properties: thus, 3-hydroxy-1-phenyl-, 4-hydroxy-1-phenyl-, and 6-hydroxy-1-phenyl-benzoxazoles do not, whereas 5-hydroxy-1-phenylbenzoxazole does show fluorescence in alkali solution; in the latter case, introduction of methyl in the 3-position enhances the fluorescence, but 3-hydroxy-1-phenyl-5-methylbenzoxazole is non-fluorescent.

Replacement of the hydroxylic hydrogen of 5-hydroxy-1-arylbenzoxazoles by methyl or ethyl gives a compound of distinct but weakened fluorescence in sulphuric acid or alcohol, and replacement of this hydrogen by acid residues produces increased weakening; further replacement in the 3-, 4-, and 6-positions usually annuls the fluorescence. With reference to Meyer's theory of the relationship between fluorescence and chemical constitution (A., 1898,

ii, 105, 275), it is found that the compounds I and II, prepared by distilling benzoyl chloride with diamino-resorcinol and -orcinol respectively, are almost devoid of



fluorescence, even in concentrated sulphuric acid solution.

Noteworthy is the occurrence of fluorescence in sulphuric acid with compounds in which the 5-position is occupied by a methyl group. Thus, 1-phenyl-5-methylbenzoxazole and 1-*o*-, 1-*m*-, and 1-*p*-tolyl-5-methylbenzoxazoles, prepared from the reduction product of the volatile mononitro-*m*-cresol, exhibit comparatively strong fluorescence in concentrated sulphuric acid.

[With GRST. OFFERMANN.]—3-Acetoxy-1-methylbenzoxazole, $C_{10}H_9O_3N$, prepared from *o*-aminoresorcinol hydrochloride and acetic anhydride, forms dense, white crystals, m. p. 68°, and shows no fluorescence in organic solvents, concentrated sulphuric acid, or potassium hydroxide solution.

3-Benzoyloxy-1-phenylbenzoxazole, $C_{20}H_{13}O_3N$, obtained by the action of benzoyl chloride on *o*-aminoresorcinol hydrochloride, forms nodular masses of needles, m. p. 143–144° with previous sintering, and yields 3-hydroxy-1-phenylbenzoxazole (Henrich and Oppermann, A., 1904, i, 934) on hydrolysis.

3-Hydroxy-1-benzylbenzoxazole, $C_{14}H_{11}O_3N$, prepared from phenylacetyl chloride and *o*-aminoresorcinol hydrochloride, forms crystals, m. p. 185°, but does not give fluorescent solutions.

5-Hydroxy-1-benzylbenzoxazole, $C_{14}H_{11}O_3N$, prepared from phenylacetyl chloride and *as*-aminoresorcinol, crystallises in white, nodular masses, m. p. 154°; its solution in alkali does not fluoresce.

5-Hydroxy-1-*o*-tolylbenzoxazole, $C_{11}H_{11}O_3N$, from *o*-toluoyl chloride and *as*-aminoresorcinol, forms crystals, m. p. 135°, and gives a pronounced green fluorescence when dissolved in alkali solution.

5-Hydroxy-1-*p*-tolylbenzoxazole forms crystals, m. p. 236–5°, and shows green fluorescence in alkali solution.

5-Hydroxy-1-benzyl-3-methylbenzoxazole, $C_{15}H_{13}O_3N$, forms crystals, m. p. 149°; its solution in dilute alkali hydroxide shows no fluorescence.

[With K. ROEDEL.]—*6-Benzoylamino-5-benzoyloxy-1-phenylbenzoxazole*, $C_{27}H_{18}O_4N_2$, prepared by the action of benzoyl chloride on the hydrochloride of diaminoresorcinol obtained by reducing dinitrosoresorcinol (Fitz, *Ber.*, 1875, **8**, 633), separates in crystals, m. p. 283° , and, when subjected to dry distillation, yields as-1:1'-*diphenylbenzodioxazole* (formula I, above), which forms pale yellow crystals, m. p. 192° , and exhibits pale blue fluorescence in concentrated sulphuric acid.

as-1:1'-*Dimethylbenzodioxazole*, $C_{10}H_8O_2N_2$, obtained from acetic anhydride and diaminoresorcinol hydrochloride, gives crystals, m. p. 192° , and is devoid of fluorescent properties in sulphuric acid.

[With F. ROSSTEUSCHER.]—*Hexa-acetyldiamino-oreinol*, $C_{19}H_{22}O_8N_2$, prepared by the action of acetic anhydride on diamino-oreinol hydrochloride, forms white crystals, m. p. $137-138^\circ$, and, when distilled in absence of solvent, yields as-1:1':4-trimethylbenzodioxazole, $C_{11}H_{10}O_2N_2$, which forms crystals, m. p. $140-141^\circ$, dissolves readily in cold concentrated sulphuric acid to a non-fluorescent solution, and forms a bromo-derivative, small needles, m. p. 233° .

[With F. ROSSTEUSCHER and N. MATULKA.]—*Benzoylamino-benzoyloxy-1-phenylmethylloxazole*, $OBz \cdot C_6HMe(NHBz) < \begin{smallmatrix} O \\ N \end{smallmatrix} > CPh$, prepared from benzoyl chloride and diamino-oreinol hydrochloride, forms colourless crystals, m. p. $246-247^\circ$, yields scarcely fluorescent solutions in alkali hydroxide solution and in sulphuric acid, and, when hydrolysed, gives *hydroxybenzoylamino-1-phenylmethylloxazole*, $C_{21}H_{18}O_3N_2$, which forms crystals, m. p. $234-235^\circ$; by alcoholic potassium hydroxide either of these compounds is apparently converted into the compound, $OH \cdot C_6HMe(NH_2) < \begin{smallmatrix} O \\ N \end{smallmatrix} > CPh$, which was not obtained in sufficient quantity for analysis. When subjected to dry distillation, benzoylamino-benzoyloxy-1-phenylmethylloxazole yields the compound, $C_{21}H_{14}O_2N_2$ (formula II, above), which crystallises in yellow needles, m. p. $189-190^\circ$, and gives a faintly fluorescing solution in sulphuric acid.

[With K. ROEDEL.]—*Aminoquinol*, $C_8H_7O_2N$, prepared by the reduction of nitroquinol (Elbs, *A.*, 1893, **i**, 640), was separated as *hydrochloride*. By benzoylation and ortho-condensation, it is converted into 4-benzoyloxy-1-phenylbenzoxazole, $C_{20}H_{13}O_3N$, which forms white crystals, m. p. 154.5° , and in sulphuric acid shows slight fluorescence; on hydrolysis it yields 4-hydroxy-1-phenylbenzoxazole, $C_{13}H_9O_2N$, crystallising in white needles, m. p. 175° , and showing a faint blue fluorescence in concentrated sulphuric acid.

[With W. WUNDER.]—*3-Aminocatechol hydrochloride*, $C_6H_7O_2N \cdot HCl$, prepared by reduction of the nitrocatechol volatile in steam (cf. Weselsky and Benedikt, *A.*, 1882, 1200), gives a dark green coloration with ferric chloride, a pale coloration with hypochlorite solution and hydrochloric acid, and a brownish-yellow coloration with potassium dichromate and sulphuric acid. Treatment with

benzoyl chloride converts it into 6-benzoyloxy-1-phenylbenzoxazole, which distils at above 400° ; 6-hydroxy-1-phenylbenzoxazole,



forms snow-white needles, m. p. $191-192^{\circ}$, and shows slight fluorescence in sulphuric acid, but not in sodium hydroxide solution.

[With N. MATULKA.]—4-Amino-m-cresol [$\text{CH}_3 : \text{OH} : \text{NH}_2 = 1 : 3 : 4$] hydrochloride (cf. von Auwers, Borsche, and Weller, this vol., i, 571) reacts (1) with benzoyl chloride, giving 1-phenyl-5-methylbenzoxazole, $\text{C}_{14}\text{H}_{11}\text{ON}$, white needles, m. p. 92.5° , which gives a highly fluorescent solution in concentrated sulphuric acid; (2) with o-toluoyl chloride, giving 1-o-tolyl-5-methylbenzoxazole, $\text{C}_{15}\text{H}_{13}\text{ON}$, which crystallises in slender, white needles with a faint odour, m. p. $94-95^{\circ}$, and forms a non-fluorescent alcoholic solution, but in concentrated sulphuric acid shows bluish-violet fluorescence; (3) with m-toluoyl chloride, giving 1-m-tolyl-5-methylbenzoxazole, colourless needles, m. p. 87° , the alcoholic solution of which shows no, and the sulphuric acid solution blue, fluorescence; (4) with p-toluoyl chloride, giving 1-p-tolyl-5-methylbenzoxazole, m. p. $117-118^{\circ}$, the sulphuric acid solution of which shows slight blue fluorescence.

T. H. P.

The Constitution of the Polysulphonated Derivatives of Indigotin. E. GRANDMOUGIN (*Compt. rend.*, 1921, 173, 586—587; cf. A., 1910, i, 74).—Indigotintetrasulphonic acid (Juillard, A., 1893, i, 348) on oxidation gives an isatindisulphonic acid in the form of its potassium salt, which when acted on by bromine in concentrated solution yields 5:7-dibromoisatin. Thus the original acid must have been indigotin-5:7:5':7'-tetrasulphonic acid. W. G.

The Mechanism of Oxidative Processes. IV. HEINRICH WIELAND (*Ber.*, 1921, 54, [B], 2353—2376).—The communication deals with (i) the oxidative decolorisation of indigotin, (ii) the oxidation of aldehydes, (iii) the catalytic decomposition of hydrogen peroxide, (iv) the peroxides as hydrogen acceptors, and (v) the biological significance of catalases.

(i) In a series of communications (A., 1913, i, 1304; 1914, i, 1007), the hypothesis has been advanced that the catalytic action of finely-divided metals in promoting oxidation is not due to activation of the oxygen, but of the hydrogen of the substrate; the process is therefore one of dehydrogenation and not of oxidation, the oxygen serving merely as acceptor for the activated hydrogen. The most marked apparent exception to this conception is the decolorisation of indigotindisulphonic acid. In extension of the observations of Kalb (A., 1910, i, 340; 1911, i, 680), however, it is now shown that indigotinsulphonic acid is converted into its dehydro-derivative by palladium black and air (the process can be arrested at this stage in pyridine, but not in aqueous solution) and that dehydroindigodatsulphonic acid is hydrolysed to isatinsulphonic acid and indigotindisulphonic acid under the experimental conditions adopted. The catalytic decolorisation of indigotin is therefore to be regarded as a case of dehydrogenation.

(ii) Further examination of the autoxidation of aldehydes has proved that the process is catalytically accelerated by animal charcoal to almost the same extent as by palladium black. Under all conditions, dry acetaldehyde absorbs oxygen to form mainly peracetic acid, whereas only acetic acid is obtained with moist acetaldehyde, pointing thus to the conclusion that it is the aldehyde hydrate which is dehydrogenated by the per-acid, $\text{CHMe}(\text{OH})_2 + \text{Me}\cdot\text{C}(\text{O})\cdot\text{O}\cdot\text{OH} = 2\text{Me}\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$. With benzaldehyde, on the other hand, much benzoic acid is formed even when every precaution to exclude moisture is observed and the process may be interpreted as follows, $\text{Ph}\cdot\text{CHO} + \text{PhC}(\text{O})\cdot\text{O}\cdot\text{OH} \rightarrow \text{PhCH}(\text{OH})\cdot\text{O}\cdot\text{O}\cdot\text{C}(\text{O})\cdot\text{Ph} \rightarrow 2\text{Ph}\cdot\text{CO}_2\text{H}$. The rate of autoxidation of salicylaldehyde is very small and is not markedly increased by the catalysts used; chloral and chloral hydrate, unfortunately, cannot be oxidised catalytically.

(iii) The decomposition of hydrogen peroxide has been shown repeatedly to be an action of the first order. According to the author's conception, however, it consists of two phases, the dehydrogenation of the first molecule which is actually observed and the immeasurably rapid reductive fission of the second molecule. $\text{HO}\cdot\text{OH} \rightarrow \text{O}\cdot\text{O} + 2\text{H}$ and $\text{HO}\cdot\text{OH} + 2\text{H} \rightarrow 2\text{H}_2\text{O}$. The whole reaction is precisely analogous to the decomposition of hydrazobenzene at its melting point, or at the atmospheric temperature in the presence of palladium black. Evidence in favour of this view is obtained by allowing the reaction to proceed in the presence of more potent hydrogen acceptors than hydrogen peroxide itself. Suitable substances are potassium persulphate in the presence of palladium black or animal charcoal, but not of blood-catalase, benzoyl peroxide which suffers reduction to benzoic acid in ethereal solution, dehydroindigotin, which is reduced to indigotin in pyridine solution by ethereal hydrogen peroxide in the presence of palladium black, and sodium nitrosodisulphonate, which is reduced to sodium hydroxylaminedisulphonate in the presence of palladium black. Blood catalase and yeast catalase are inactive towards dehydroindigotin and sodium nitrosodisulphonate.

(iv) Hydrogen peroxide can behave as a hydrogenating agent by loss of hydrogen and liberation of molecular oxygen, as a dehydrogenating agent by reacting with hydrogen and, in many reactions, as a true oxidising agent. The di-secondary peroxides can exhibit only the second type of action. It is shown in the case of potassium persulphate, dibenzoyl peroxide, and diethyl peroxide that they can behave as acceptors in catalytically accelerated dehydrogenations, quinol being used as substrate. The powerful catalytic action of animal charcoal in the reactions with persulphate and benzoyl peroxide is remarkable; there can be no doubt that in this case, as with palladium black, the adsorbed quinol suffers a change in its structure which is manifested by the less firm union of its hydrogen atoms. Blood catalase also greatly accelerates the dehydrogenation of quinol by potassium persulphate. Acetaldehyde and potassium persulphate do not react with one

another in 1% solution; the dehydrogenation of the aldehydehydrate is, however, with persulphate as acceptor, accelerated by palladium black, as is also that of dextrose.

(v) The processes which consume oxygen and occur in the living cell are not to be explained by enzymatic activation of molecular oxygen but by activation of the hydrogen in the substance which suffers combustion. The hypothesis is supported by evidence drawn from the work of Thunberg (A., 1920, i, 784), Lipschitz (this vol., i, 203), and Batelli and Stern (*Chem. Zentr.*, 1921, i, 581).
H. W.

The Constitution of Isatin Salts and Isatol. GUSTAV HEILER (*Ber.*, 1921, 54, [B], 2214—2222).—A reply to the recent criticism of Hantzsch (this vol., i, 597) on the author's work in the isatin series.

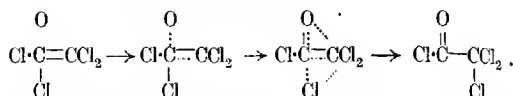
It is pointed out that Hantzsch's view of the non-existence of isatin *N*-salts is mainly supported by arguments based on the behaviour of ethyl acetoacetate and similar tautomeric substances. The comparison is, however, scarcely valid, since, in general, such isomerism in cyclic systems leads to the development of phenolic character and consequently of acidic properties in the lactim form, —N:C(OH)— . In the ring system of isatin lactim, however, the hydroxyl under the influence of the nitrogen atom has no actual phenolic character, but behaves more nearly as a tertiary alcoholic group which is susceptible of alkylation to a readily-hydrolysed ether, but does not allow the replacement of the hydrogen atom by alkali.

With regard to practical details, the production of isatol from isatin silver and benzoyl chloride is again confirmed, and the uniformity of the product is established by crystallographic measurements. Contrary to Hantzsch's assumption, a comparison of the physical and chemical properties of isatol and methylisatoid of von Baeyer and Ökonomidis shows that these substances are not identical. Hantzsch's statement that methylisatoid does not contain the methyl group since it can also be prepared from isatin silver and ethyl iodide is not supported by the author's experiments, since he finds the ethylisatoid thus formed to differ from methylisatoid.
H. W.

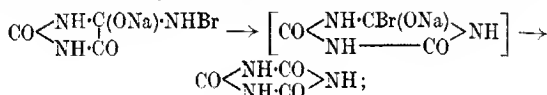
Explanation of certain Transformations of Oxonic Acid and of Allantoxaidin. HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1921, 54, [B], 2441—2448).—Oxonic acid, the identity of which with allantoxanic acid was demonstrated by the authors (A., 1920, i, 885), and also allantoxaidin may be readily converted into cyanuric acid and into biuret. The yields are good, but it is not easy to explain by simple reactions the opening of the 4:5-carbon-carbon linking, as similar linkings in other analogous compounds show great stability. The following results furnish the explanation required.

The oxidations of oxonic acid and allantoxaidin to cyanuric acid by acid permanganate solution or other oxidising agent are examples of oxidation rearrangements (Biltz, A., 1913, i, 241)

analogous to the oxidation of bisdiphenylene-ethylene to diphenylphenanthrene (Klinger and Lonnes, A., 1896, i, 691). The similar oxidation of tetrachloroethylene to trichloroacetyl chloride (Biltz, A., 1902, i, 417) may be represented thus :

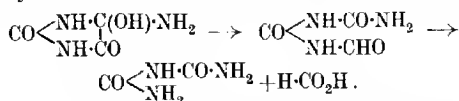


According to this view, allantoxaidin should exhibit combining power at the carbon-nitrogen pair united by a double linking. It is, indeed, found that allantoxaidin unites with sodium hypobromite, the bromine atom passing to the 6-nitrogen atom and the ONa group to the 5-carbon atom. By the action of acetic acid on the resulting compound, the sodium may be replaced by a hydrogen atom, giving 5-bromoamino-5-hydroxyhydantoin. The latter, and also its sodium derivative, undergoes even in the cold, although more rapidly on heating, a species of Hofmann's reaction, with formation of cyanuric acid :



the intermediate product assumed cannot, however, be isolated. The transformation of *cyclopentanoxime* into α -piperidone, that of oximinocamphor into camphorimide, and many other similar ring-enlargements are known. This formation of cyanuric acid from allantoxaidin furnishes support for Ponomareff's formula for allantoxaidin (A., 1879, 227, 461) the reaction being inexplicable on the basis of the constitution $\text{CO} \begin{array}{c} \text{N}=\text{C} \cdot \text{NH}_2 \\ \text{NH} \cdot \text{CO} \end{array}$.

The decomposition of allantoxaidin into biuret and formic acid when heated in aqueous solution, either alone or with acid, may be explained if it is assumed that the molecule of water of crystallisation is combined by the allantoxaidin with formation of 5-amino-5-hydroxyhydantoin. The latter contains hydroxyl and carbonyl oxygen at two adjacent carbon atoms, and, like many analogous compounds, such as lactic acid, which decomposes into acetaldehyde and formic acid, shows a tendency to undergo fission :



The formation of biuret as well as of cyanuric acid when 5-bromoamino-5-hydroxyhydantoin is heated in aqueous solution is explained thus : the hydrogen bromide produced by the formation of cyanuric acid reacts with other molecules causing scission of hypobromous acid and reacts with this, liberating bromine, the

allantoxaidin thus set free then undergoing conversion into biuret; this view is confirmed by the observation that no biuret is formed when excess of hypobromite is present in the solution.

5-Bromoamino-5-hydroxyhydantoin, $C_2H_3O_3N_2Br$, forms poorly-developed crystals, m. p. about 143° (decomp.), and its sodium derivative, colourless needles. T. H. P.

3-Methyloxonic Acid and 3-Methylallantoxaidin. HEINRICH BILTZ and RUDOLF ROBL (*Ber.*, 1921, **54**, [B], 2448—2451).—The conversion of allantoin into oxonic (allantoxanic) acid and allantoxaidin finds a parallel in that of 3-methylallantoin (Behrend and Zieger, A., 1916, i, 164) into 3-methyloxonic acid and 3-methylallantoxaidin. The dimethylallantoxaidin obtained from diazomethane and allantoxaidin (A., 1920, i, 886) has m. p. 164° and not 158° as previously given; since treatment of 3-methylallantoxaidin with diazomethane yields the same dimethyl derivative, one of the methyl groups of the latter must occupy the 3-position, but for the other methyl no choice is yet possible between the 1- and 6-positions.

3-Methyloxonic (3-methylallantoxanic) acid, $CO \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{N} \cdot \text{CO}_2\text{H} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix}$,

forms short, indistinct crystals and loses carbon dioxide when heated, its apparent melting point being that of 3-methylallantoxaidin. It is obtained as the potassium salt when 3-methylallantoin is oxidised by permanganate in alkaline solution.

3-Methylallantoxaidin, $CO \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{NH} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix}$, crystallises in elongated

prisms with oblique or roof-shaped ends, sintering at about 200° , m. p. 226° . Its conversion into α -methylbiuret has not yet been achieved.

An unsuccessful attempt has been made to transform 1-methylallantoin into 1-methyloxonic acid. T. H. P.

Allantoin and its Methyl Derivatives. HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1921, **54**, [B], 2451—2476).—When subjected to prolonged boiling in aqueous solution, uric acid-4:5-glycol dimethyl ether yields allantoin, and similar behaviour is shown by the corresponding derivatives of various alkylated uric acids, although some of these either remain unchanged or give only the mono-ethers of the glycols. Thus, the glycol ethers of 1- and 7-methyluric acids yield 3-methylallantoin; that of 7-ethyluric acid, 3-ethylallantoin; those of 1:3- and 7:9-dimethyluric acids, 1:3-dimethylallantoin, and that of 1:7-dimethyluric acid, 3:8-dimethylallantoin. The glycol dimethyl ether of 3:7-dimethyluric acid gives the monomethyl ether, whilst those of 3:9-dimethyl-, 1:3:7-trimethyl-, and tetramethyl-uric acids remain unchanged. These glycols may undergo cafolide degradation, 3:7-dimethyluric acid-glycol, for instance, yielding 1-methyl-5-hydroxyhydantoylamide. The transformation of the uric acid-glycol ethers into allantoin may be accelerated by dissolving the ethers in alkali hydroxide solution, acidifying the solutions, and crystallising.

The various explanations which have been advanced of the mechanism of the formation of allantoin by the oxidation of uric acid in presence of alkali are discussed, the conclusion being drawn that the first and only intermediate product in this oxidation is hydroxyacetylenediureinecarboxylic acid (Behrend, A., 1904, i, 950). If the resulting strongly alkaline liquid is concentrated by evaporation, even in the cold, potassium uroxanate crystallises out, this compound being formed by simple hydrolysis. If, however, the solution of the hydroxyacetylenediureinecarboxylic salt is acidified, the free acid loses its carboxyl group. The one ring, if possible that free from methyl groups, then appears to undergo immediate opening, displacement rearrangement giving the allantoin. The acidification is best effected by means of a weak acid, such as acetic acid, since evaporation of allantoin in presence of mineral acid results in its decomposition.

As regards the structure of allantoin, all the facts known previously, and likewise the results now obtained for the first time, are in complete agreement with the formula proposed by Grimaux (A., 1877, ii, 741), and Fenton and Wilks's reaction with monomethylfuryl (A., 1911, i, 269) also appears to support an open-chain formula. The available data are reconcilable with the hydroxyacetylenediureine formula only with difficulty, if at all. The optical inactivity always exhibited by allantoin may be due to extremely rapid racemisation.

3-Ethylallantoin, $\begin{array}{c} \text{CO}\cdot\text{NH} \\ \text{N}\cdot\text{Et}\cdot\text{CO} \end{array} > \text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared by boiling

an aqueous solution of 4 : 5-dimethoxy-7-ethyl-4 : 5-dihydrouric acid (Biltz, Marwitzky, and Heyn, this vol., i, 606), crystallises in long, slender prisms with roof-like ends, m. p. 189—190° (slight frothing), and yields 3-ethylhydantoin when reduced by means of hydriodic acid.

1 : 3-Dimethylallantoin, $\begin{array}{c} \text{CO}\cdot\text{NMe} \\ \text{N}\cdot\text{Me}\cdot\text{CO} \end{array} > \text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in

the triclinic system, in either rectangular prisms or flat, quadrilateral, double pyramids with truncated apices [S. RIEDEL: $a:b:c=2.398:1:1.306$; $\alpha=89^\circ 7'$, $\beta=94^\circ 5'$, $\gamma=98^\circ 58'$], m. p. 214°, and yields 1 : 3-dimethylhydantoin on reduction by means of hydriodic acid.

5-Hydroxy-1-methylhydantoinamide, $\text{C}_5\text{H}_7\text{O}_4\text{N}_3$, obtained when an aqueous solution of 4 : 5-dihydroxy-3 : 7-dimethyl-4 : 5-dihydrouric acid is boiled, crystallises in stout, mostly hexagonal plates [BEUTEL: apparently monoclinic], m. p. 203—204° (frothing and yellowing), and gives methylparabanic acid in good yield when oxidised.

1 : 8-Dimethylallantoin, $\begin{array}{c} \text{CO}\cdot\text{NMe} \\ \text{NH}\cdot\text{CO} \end{array} > \text{CH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$, prepared

by heating an aqueous solution of 1 : 7-dimethylspirodihydantoin with basic lead acetate, forms stout, hexagonal crystals, m. p. 220—223° (evolution of gas and darkening), and is reduced to 1-methylhydantoin by hydriodic acid.

1:3:8-Trimethylallantoin, $C_7H_{12}O_3N_4$, prepared by the prolonged action of diazomethane on 1:8-dimethylallantoin, crystallises in narrow, flat prisms, sintering at 149° , m. p. 152° , and gives 1:3-dimethylhydantoin when treated with hydriodic acid.

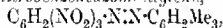
Methylation of 1:6-dimethylallantoin by means of diazomethane yields 1:3:6-trimethylallantoin.

T. H. P.

Stability of Uric Acid-Glycol Dimethyl Ether. HEINRICH BILTZ and FRITZ MAX (*Ber.*, 1921, **54**, [B], 2477–2479).—That certain samples of uric acid-4:5-glycol dimethyl ether (4:5-dimethoxy-4:5-dihydrouric acid) (cf. Biltz and Heyn, A., 1917, i, 286) yield, on prolonged boiling in aqueous solution, not allantoin, but uric acid-4:5-glycol monomethyl ether is found to be due to the fact that the dimethyl ether is not so stable as was previously thought and undergoes rapid transformation into 5-methoxy- ψ -uric acid if a small proportion of the hydrochloric acid formed during its preparation is left with the ether as impurity.

T. H. P.

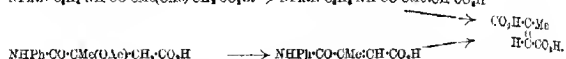
The Coupling of Benzenoid Hydrocarbons with Diazo-compounds. KURT H. MEYER and HANS TOCHTERMANN (*Ber.*, 1921, **54**, [B], 2283–2285).—It has been shown previously (A., 1920, i, 97) that unsaturated aliphatic hydrocarbons couple with diazo-compounds to give crystalline azo-derivatives, but similar compounds have not been obtained previously with aromatic hydrocarbons, probably because the reaction occurs so slowly that the diazonium salt is decomposed before it has proceeded to a reasonable degree. It is now shown that the unusually reactive diazotised 2:4:6-trinitroaniline (prepared under the conditions described by Misslin, A., 1920, i, 887) couples readily with mesitylene to form 2:4:6-trinitrobenzenediazomesitylene,



dark red, hexagonal platelets, m. p. 189° (decomp.), the constitution of which is deduced from its reduction to mesitylamine. Misslin's solution gives immediate intense colorations with toluene, *m*-xylene, α -methylnaphthalene, and anthracene which doubtless depend on the formation of azo-compounds, but the relative slowness of the action inhibits the isolation of the products; benzene, on the other hand, does not give a coloration.

H. W.

Isonitriles. II. Compounds with Aldehydes or Ketones and Monobasic Organic Acids. M. PASSERINI (*Gazzetta*, 1921, **51**, ii, 181–188).—It has been shown (this vol., i, 743) that *p*-carbaminoazobenzene reacts with acetone and acetic acid, giving rise to the acetyl derivative of hydroxyisobutyl-*p*-aminoazobenzene. It is now found that a precisely similar reaction occurs with benzaldehyde, benzoic acid, and an isonitrile. The reaction may, indeed, be regarded as general, the compound obtained undergoing progressive hydrolysis in accordance with the scheme: $NHR \cdot CO \cdot CR' \cdot R'' \cdot O \cdot CO \cdot R'''$ (when an aldehyde is used, $R' = H$) \longrightarrow $NHR \cdot CO \cdot CR' \cdot R'' \cdot OH \longrightarrow CO_2H \cdot CR' \cdot R'' \cdot OH$.

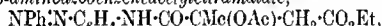
$$\text{NPh}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CMe}(\text{O}i\text{c})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{Et} \rightarrow \text{NPh}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CMe}(\text{OH})\cdot\text{CO}\cdot\text{H}$$


Benzoyloxyphenylacetyl-p-aminoazobenzene,



Mandelyl-p-aminoazobenzene, $\text{NPh:N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CHPh}\cdot\text{OH}$, which crystallises in lustrous, copper-red scales, m. p. 186—188°.

Ethyl β-p-aminoazobenzeneacetulcitramalate.



obtained from ethyl acetoacetate, *p*-carbylaminoazobenzene, and acetic acid, crystallises in silky, yellow needles, m. p. 141°, and, when cautiously hydrolysed, yields either β -*p*-aminoazobenzene-*mesa*conic or β -*p*-aminoazobenzene-*citraconic* acid, $C_{17}H_{15}O_3N_3$ (see above), as a yellow precipitate, m. p. 179°.

β -Anilinoacetylcitraconic acid, $\text{NHPh-CO-CMe(OAc)-CH}_2\text{-CO}_2\text{H}$, forms crystals, m. p. 77–78°, and as first product of hydrolysis yields β -anilinoisocitraconic or β -anilinoitraconic acid, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$ (see above), crystallising in stout, highly refractive prisms, m. p. 165°. Two compounds different from each other and from that now obtained have been described as anilinoisocitraconic acid (cf. Michael and Palmer, A., 1886, 698; Anschütz and Reuter, A., 1890, 368).

T. H. P.

Azo-compounds from Diketohydrindene. A. K. DAS and B. N. GHOSH (*J. Amer. Chem. Soc.*, 1921, **43**, 1739—1741).—Azo-compounds are formed by coupling diazonium compounds with 1:3-diketohydrindene in alkaline solution. The products

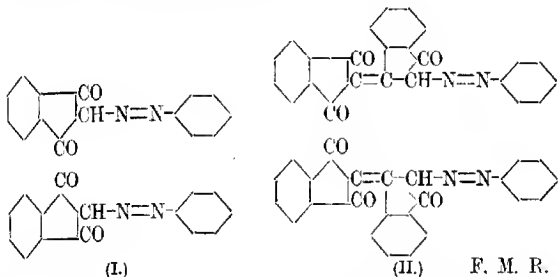
form insoluble sodium salts, but when applied to vegetable fibres in the usual manner for the production of insoluble azo-colours on the fibre fast shades are produced.

p-Nitrobenzeneazo-1:3-diketohydrindene, yellow crystals from pyridine, does not melt below 280°, and dissolves in sulphuric acid with a red colour and in potassium hydroxide with a magenta colour.

p-Tolueneazo-1:3-diketohydrindene, yellow, silky flakes from acetic acid, m. p. 211°, dissolves in sulphuric acid with a chocolate colour.

β -Naphthaleneazo-1:3-diketohydrindene, m. p. 205°, from acetic acid.

1:3-Diketohydrindene is readily converted into anhydro-bis-diketohydrindene. Thus, when tetrazotised benzidine is coupled with an alkaline solution of two molecular proportions of 1:3-diketohydrindene below 5°, *diphenylbisazo-1:3-diketohydrindene* (I) is formed, whereas when the coupling is effected at 26°, *diphenylenebisazo-anhydro-bisdiketohydrindene* (II) is formed.



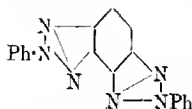
pseudoAzimides. I and II. MAXIMILIAN P. SCHMIDT and ALFRED HAGENBÜCKER (*Ber.*, 1921, **54**, [B], 2191—2200, 2201—2209).—I. *o*-Aminoazo-compounds are readily oxidised to *pseudo*-azimides, but this behaviour is not shown by those substances which contain a further amino-group in the molecule. It is now shown that in these cases oxidation can be effected smoothly by ammoniacal cupric oxide solution, but it is noteworthy that four molecules of the oxidising agent are required for one molecule of dye instead of the two molecules calculated on the assumption of reduction to the cuprous stage.

5-Amino-2-phenyl-1:2:3-benztriazole, m. p. 182.5°, is obtained by boiling a suspension of benzeneazo-*m*-phenylenediamine in alcohol (50%) with an aqueous solution of copper sulphate which has been treated with excess of ammonia. Similarly, benzeneazo-*m*-tolenylenediamine is transformed into 5-amino-2-phenyl-6-methyl-1:2:3-benztriazole, $\text{NH}_2\text{-C}_6\text{H}_2\text{Me}<\text{N}>\text{NPh}$, m. p. 215°, and

p-sulphobenzeneazo-*m*-phenylenediamine yields the sodium salt of 5-amino-2-sulphophenyl-1:2:3-benztriazole, needles which give an intense, yellowish-green, fluorescent solution (the corresponding acid is described). *p*-Nitrobenzeneazo-*m*-phenylenediamine, long,

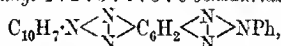
red needles, m. p. 230°, is converted by copper sulphate in boiling aqueous pyridine solution into 5-amino-2-p-nitrophenyl-1:2:3-benzotriazole, $\text{NH}_2\cdot\text{C}_6\text{H}_3\langle\text{N}\rangle\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, long, reddish-brown

needles, m. p. 331°, which is reduced by zinc dust and glacial acetic acid to 5-amino-2-p-aminophenyl-1:2:3-benzotriazole, m. p. 194°, which can be diazotised in the usual manner and couples normally with diazonium compounds (the hydrochloride, sulphate, and acetyl derivatives are described). 5-Amino-2-phenyl-1:2:3-benzotriazole couples with benzenediazonium chloride to yield 4-benzeneazo-5-amino-2-phenyl-1:2:3-benzotriazole, needles, m. p. 112° (the

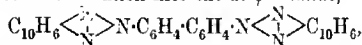


hydrochloride is described); the position of the azo-group is deduced from the similarity of the parent substance to β-naphthylamine. The dye is oxidised by lead peroxide in boiling xylene solution to 2:5-diphenyl-1:2:3:4:5:6-benzoditriazole (annexed formula), four-sided, silvery plates or aggregates of needles, m. p. 221°. 5-Amino-2-sulphophenyl-1:3-benzotriazole couples with diazotised sulphanilic acid, giving the sodium salt of 4-p-sulphobenzeneazo-5-amino-2-p-sulphophenyl-1:2:3-benzotriazole, $\text{C}_{18}\text{H}_{12}\text{O}_6\text{N}_6\text{S}_2\text{Na}_2$, which is oxidised by ammoniacal copper solution to the sodium salt of 2:5-di-p-sulphophenyl-1:2:3:4:5:6-benzoditriazole, $\text{C}_{18}\text{H}_{10}\text{O}_6\text{N}_6\text{S}_2\text{Na}_2$. 2-Phenyl-1:2:3-benzotriazole-5-azo-β-naphthylamine (from diazotised 5-amino-2-phenyl-1:2:3-benzotriazole and β-naphthylamine), small needles, m. p. 258°, is oxidised by lead peroxide in boiling xylene solution 5(2':1':3'-naphthtriazolyl)-

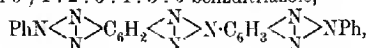
2-phenyl-1:2:3-benzotriazole, $\text{C}_{10}\text{H}_6\langle\text{N}\rangle\text{N}\cdot\text{C}_6\text{H}_3\langle\text{N}\rangle\text{N}\cdot\text{NPh}$, silvery scales, m. p. 235°. Similarly, 4-β-naphthaleneazo-5-amino-2-phenyl-1:2:3-benzotriazole, tile-red needles, m. p. 155–158°, gives 2-phenyl-5-β-naphthyl-1:2:3:4:5:6-benzoditriazole,



m. p. 220°. Tetrazotised benzidine and β-naphthylamine give the compound, $\text{C}_{33}\text{H}_{24}\text{N}_6$, needles of metallic lustre, m. p. 315° (the corresponding sulphate is described), which is converted by copper powder or, but less advantageously, by lead peroxide in boiling nitrobenzene solution into the di-ψ-azimide,



colourless leaflets, m. p. 317°. The substance, $\text{C}_{21}\text{H}_{12}\text{N}_6$, tile-red crystals, m. p. 245° (decomp.), obtained by coupling 2-phenyl-1:2:3-benzotriazole-5-diazonium sulphate with 5-amino-2-phenyl-1:2:3-benzotriazole, is oxidised to 2-phenyl-5-(2'-phenyl-1':2':3'-benztriazolyl-5')-1:2:3:4:5:6-benzoditriazole,

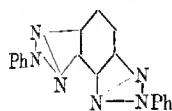


small leaflets, m. p. 231°.

II. *m*-Phenylenediamine readily couples with two molecules

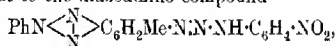
of a diazonium compound with the formation of bisazo-dyes, but the point of attachment of the second diazonium residue has not been placed beyond doubt. Since the dyes do not suffer fission in the normal manner, the authors have endeavoured to elucidate the problem by converting them into ditriazoles. It is found that the "double coupling" of *m*-phenylenediamine takes place in a more complex manner than was previously supposed and that, under the customary conditions of the reaction, the second diazonium residue becomes attached in about an equal degree to the 2- and 6-positions of *m*-phenylenediamine, thus yielding two bisazo-dyes which are oxidisable to two ditriazoles.

It has been shown already that the azo-dye derived from benzenediazonium chloride and 5-amino-2-phenyl-1:2:3-benztriazole is oxidised to an *o*-benzditriazole which must have the annexed



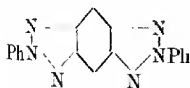
formula if the diazonium residue enters the molecule in position 4. This was considered to be the case by reason of the similarity of the amine to β -naphthylamine, but a more definite proof is obtained in the following manner. 5-Amino-2-phenyl-6-methyl-1:2:3-

benztriazole reacts with benzenediazonium chloride to form 4-benzeneazo-5-amino-2-phenyl-6-methyl-1:2:3-benztriazole, yellowish-red crystals, m. p. 165°, in which the new group must have entered in position 4, since coupling in the meta-position has never been observed. If, however, the position 4' is occupied by a methyl group as in 5-amino-2-phenyl-4-methyl-1:2:3-benztriazole, coarse prisms, m. p. 126° (obtained by the oxidation of 3-benzeneazo-2:6-tolylenediamine, needles, m. p. 124°), the action of a diazotised solution of *p*-nitroaniline does not lead to the production of an azo-dye but to the diazoamino-compound



which is converted by concentrated sulphuric acid into *p*-nitroaniline and 2-phenyl-4-methyl-1:2:3-benztriazole-5-diazonium sulphate.

The action of benzenediazonium chloride on benzeneazo-*m*-phenylenediamine leads to the formation of a mixture of 2:4-dibenzeneazo-*m*-phenylenediamine, m. p. 250° (discovered by Griess), and 2:6-dibenzeneazo-*m*-phenylenediamine, red needles, m. p. 159°; the constitution of the former is deduced from the observation that it is converted by copper sulphate in aqueous pyridine solution



into a ditriazole which is not identical with the ortho-compound described above and which therefore must be 2:6-di-phenyl-1:2:3:5:6:7-benzditriazole (annexed formula), m. p. 334°, whereas the

isomeride, m. p. 159°, is transformed into 2:5-diphenyl-1:2:3:4:5:6-benzditriazole, m. p. 221°.

3:5-Dibenzeneazo-2:4-tolylenediamine, long, red needles, m. p. 135° (from benzeneazotolylenediamine and benzenediazonium chloride), is oxidised by copper sulphate in aqueous pyridine

solution to 2:5-diphenyl-7-methyl-1:2:3:4:5:6-benzdiazole, m. p. 192°, which is also obtained by the action of lead peroxide on 4-benzencazo-5-amino-2-phenyl-6-methyl-1:3-benztriazole in boiling xylene. H. W.

Azides of Thiocarbamic Acids. E. OLIVERI-MANDALÀ (*Gazzetta*, 1921, 51, ii, 195—201).—In conjunction with Noto, the author has shown (A., 1913, i, 774) that the action of azoimide on phenylthiocarbimide at 40° yields the compound described by Freund and Hempel (A., 1895, i, 193) as 3-thio-4-phenyltetrazoline. This compound does not, however, correspond in chemical behaviour with such a structure and the author regards it as the azide of phenylthiocarbamic acid, $\text{NHPh}\cdot\text{CS}\cdot\text{N}_3$, analogous to the azides of carbamic acid. The mechanism of the addition of azoimide to thiocarbimides would then be similar to that of its addition to carbimides and to ketens: $\text{R}\cdot\text{N}\cdot\text{C}\cdot\text{S} + \text{N}_3\text{H} = \text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{N}_3$, $\text{R}\cdot\text{N}\cdot\text{C}\cdot\text{O} + \text{N}_3\text{H} = \text{R}\cdot\text{NH}\cdot\text{CO}\cdot\text{N}_3$ and $\text{R}_2\cdot\text{C}\cdot\text{C}\cdot\text{O} + \text{N}_3\text{H} = \text{R}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{N}_3$. Further, the reaction between nitrous acid and a thiosemicarbazide, $\text{NHR}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}_2 + \text{HNO}_2 \rightarrow \text{NHR}\cdot\text{CS}\cdot\text{N}_3$, becomes analogous to Curtius's reaction between nitrous acid and a semicarbazide. Again, just as Curtius and Burkhardt (A., 1899, i, 137) observed with azides of the carbamic acids, these azides of thiocarbamic acids are found to lose their triazo-group as azoimide when treated with ammonia, aniline, or phenylhydrazine, derivatives of thiocarbamide being thus formed. On the other hand, the azides of thiocarbamic acids are distinguished from those of carbamic acids by the great mobility of their triazo-groups. Thus, alkalis convert them into isomeric tetrazole derivatives, $\text{NHR}\cdot\text{CS}\cdot\text{N}_3 \rightarrow \begin{smallmatrix} \text{NR} & \text{N} \\ & \diagdown \quad \diagup \\ & \text{C}(\text{SH}) & \text{N} \end{smallmatrix}$, whilst treatment with hydrochloric acid results in the loss of two nitrogen atoms from the molecule and heating in an indifferent solvent in the elimination of an atom of sulphur, $\text{NHR}\cdot\text{CS}\cdot\text{N}_3 \rightarrow \text{NHR}\cdot\text{C} \begin{smallmatrix} \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \rightarrow \text{NHR}\cdot\text{CN}$.

The azide of phenylthiocarbamic acid yields phenylthiocarbamide when treated with concentrated aqueous ammonia, and diphenylthiocarbamide when treated with alcoholic aniline.

The azide of *o*-tolylthiocarbamic acid, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CS}\cdot\text{N}_3$, prepared from *o*-tolylthiocarbimide and azoimide, crystallises in large, thin plates, m. p. 120° (decomp.), and is highly sensitive to the action of light, which gradually turns it red. When heated with alcoholic ammonia under pressure, it gives *o*-tolylthiocarbamide, $\text{C}_6\text{H}_7\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, which forms crystals, m. p. 154—155°.

1-*o*-Tolyltetrazole-5-thiol, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N} \begin{smallmatrix} \diagup \quad \diagdown \\ \text{C}(\text{SH}) & \text{N} \\ \text{N} & \text{N} \end{smallmatrix}$, obtained by isomeric change of the preceding compound under the action of alkali, forms crystals, m. p. 129°. When oxidised by means of ferric chloride in alcoholic solution, it appears to yield the disulphide, $\text{C}_6\text{H}_7\cdot\text{CN}_4\cdot\text{S}\cdot\text{S}\cdot\text{CN}_4\cdot\text{C}_6\text{H}_7$, which was not isolated owing to lack of material. By alkaline permanganate solution it is, however, converted in the cold into 1-*o*-tolyltetrazole-5-sulphonic acid,

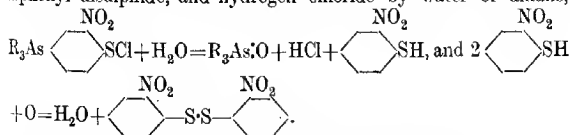
$C_7H_7 \cdot CN_4 \cdot SO_3H$, which was isolated as the *potassium* salt, and in the hot into 5-hydroxytetrazole-1-benzoic acid, $CO_2H \cdot C_6H_4 \cdot CN_4 \cdot OH$, which begins to decompose slowly when heated above 200° and in appearance closely resembles its *para*-isomeride (*loc. cit.*).

T. H. P.

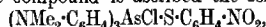
Action of Sulphur Monochloride on Tertiary Aromatic Arsines: Constitution of Sulphur Monochloride. FRITZ ZUCKERKANDL and MARTHA SINAI (*Ber.*, 1921, 54, [B], 2479—2489).—The action of sulphur monochloride on tertiary aromatic arsines, which, if similar to that on triphenylbismuthine (Challenger, T., 1916, 109, 250), might be used for the preparation of arsine dichlorides not obtainable by the action of chlorine on tertiary arsines, actually proceeds quite differently. In an indifferent solvent, the reaction yields an additive compound, $AsR_3 \cdot S_2Cl_2$, which is instantly decomposed by water or alkali, $AsR_3 \cdot S_2Cl_2 + H_2O = 2HCl + S_2 + R_3As \cdot O$, and is converted into the corresponding sulphide, $R_3As \cdot S$, by either hydrogen sulphide or ammonium pentasulphide.

This new method for obtaining tertiary aromatic arsine oxides and sulphides has been applied to the preparation of triphenylarsine hydroxide and sulphide, tri- α -naphthylarsine hydroxide (Michaelis, A., 1902, i, 517, 524), tri- α -naphthylarsine sulphide, *pp'p''*-hexamethyltriaminotriphenylarsine oxide and sulphide. The additive compounds with sulphur chloride vary greatly in stability, but they need not be isolated, and the yields of arsine oxide and sulphide are very good. That such compounds are actually additive and not merely molecular in character is shown by the fact that they always decompose into derivatives of quinquivalent arsenic.

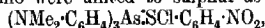
Of the three possible structures for such additive compounds, namely, $AsR_3 \cdot S \cdot SCl_2$, $AsR_3Cl \cdot S \cdot SCl$, and $AsR_3(SCl)_2$, the second is regarded as the most probably accurate (cf. Lecher, A., 1920, i, 433; von Konek, A., 1920, i, 880), this involving the assumption that sulphur chloride has the simple disulphide formula, $Cl \cdot S \cdot S \cdot Cl$. That such assumption is justified is shown by the interaction of *o*-nitrophenylsulphur chloride, $NO_2 \cdot C_6H_4 \cdot S \cdot Cl$ (Zincke and Farr, A., 1912, i, 763) on *pp'p''*-hexamethyltriaminotriphenylarsine, which also yields an additive compound, decomposed immediately into hexamethyltriaminotriphenylarsine oxide, *oo'*-dinitrodiphenyl disulphide, and hydrogen chloride by water or alkalis,



To the additive compound is ascribed the formula



since if the chlorine were united to sulphur as in



the action of water should yield *o*:*o'*-dinitrodiphenylsulphur oxide,

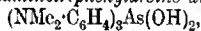
$O(S-C_6H_4 \cdot NO_2)_2$, or even the corresponding disulphoxide or sulphinic acid, $NO_2 \cdot C_6H_4 \cdot SO_2H$; such sulphur oxides are formed, for instance, by the action of water or alkali on *o*-nitrophenylsulphur chloride (Zincke and Farr, *loc. cit.*).

It has not been found possible to prepare the intermediate product, $PPh_3Cl \cdot S \cdot S \cdot Cl$, from triphenylphosphine (Pfeiffer, Hiller, and Pietsch, A., 1905, i, 164). This result conforms exactly with Steinkopf and Buchheim's observation that tertiary arsines combine with cyanogen bromide to form relatively stable arsinebromocyanides, whereas the corresponding compound formed by triphenylphosphine is unstable and could not be isolated (this vol., i, 469).

The *additive* compound, $AsPh_3Cl \cdot S \cdot S \cdot Cl$, formed by triphenylarsine and sulphur chloride, forms yellowish-white crystals, m. p. 200° , a minimal addition of free sulphur lowering the melting point to below 110° ; when boiled with ammonia solution, triphenylarsine hydroxide is formed.

The *additive* compound, $(NMe_2 \cdot C_6H_4)_3AsCl \cdot S \cdot S \cdot Cl$, obtained from *pp'*-hexamethyltriaminotriphenylarsine and sulphur chloride, forms crystals, m. p. $137-141^\circ$.

pp'-Hexamethyltriaminotriphenylarsine dihydroxide,



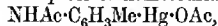
crystallises in cubes, m. p. 257° . The corresponding *oxide*, $(NMe_2 \cdot C_6H_4)_3As \cdot O$, forms white crystals, m. p. 277° , and the *sulphide*, $C_{24}H_{30}N_3As$, glistening leaflets, m. p. $269-270^\circ$.

The *additive* compound, $(NMe_2 \cdot C_6H_4)_3AsCl \cdot S \cdot C_6H_4 \cdot NO_2$, formed by hexamethyltriaminotriphenylarsine and *o*-nitrophenylsulphur chloride, forms crystals, m. p. 201° (decomp.).

Tri-*α*-naphthylarsine, obtained by Michaelis (*loc. cit.*) in 20% yield, may be obtained in 46% yield from *α*-bromonaphthalene, magnesium, and arsenic trichloride. The *additive* compound with sulphur chloride, $C_{30}H_{21}Cl_2S_2As$, forms crystals, m. p. 175° (decomp.). Tri-*α*-naphthylarsine dihydroxide and the *sulphide*, $As(C_{10}H_7)_3S_2$, which forms white leaflets, m. p. 285° , were prepared. T. H. P.

Action of Mercuric Acetate on *p*-Toluidine. II. L. VECCHIOTTI (*Gazzetta*, 1921, 51, ii, 208-210).—In order to ascertain the position of the mercury group in the molecule of *p*-toluidine-mercuriacetate (A., 1919, i, 103) in relation to the amino-group, the author acetylates the latter and treats the acetyl derivative with bromine in acetic acid solution, the resulting product being *m*-bromo-*p*-acetotoluidide, m. p. 118° (Wroblewsky, *Annalen*, 1861, 118, 152). Thus, when the para-position is occupied by either mercury or methyl, a second mercury atom entering the nucleus always goes to the ortho-position with reference to the amino-group.

The *acetyl* derivative of *p*-toluidine-mercuriacetate,



forms colourless, highly refractive, prismatic crystals, m. p. 175° .

T. H. P.

Complex Salts of Mercury with Phenols. V. PAOLINI (*Gazzetta*, 1921, 51, ii, 188-194).—According to Merck (*Arch.*

Pharm., 1893, 231, 124), the compound obtained by the interaction of thymol and mercuric acetate consists of two molecules of mercuric acetate, in one of which one of the acetyl groups is replaced by a thymyl residue, $\text{Hg}(\text{OAc})_2 + \text{OAc} \cdot \text{Hg} \cdot \text{O} \cdot \text{C}_{10}\text{H}_{13}$. The existence of such compounds is, however, doubtful, and their constitution cannot be determined by their elementary composition alone (Schmidt, *Pharmazeutische Chemie*, 1911, ii, 1099). The author has prepared a mercuric acetate-thymol compound which contains non-ionisable mercury united directly to the carbon of the nucleus, the compound being readily and completely soluble in dilute sodium hydroxide and precipitated unchanged on addition of an acid. Treatment of this compound with aqueous sodium chloride yields the corresponding mercuric chloride compound, from which the two HgCl residues are displaced by two iodine atoms when the compound is treated with a solution of iodine in aqueous potassium iodide. The formation of the original compound and these transformations are represented by the equations: $\text{OH} \cdot \text{C}_6\text{H}_3\text{MePr} + 2\text{Hg}(\text{OAc})_2 = 2\text{AcOH} + \text{OH} \cdot \text{C}_6\text{HMePr}(\text{Hg} \cdot \text{OAc})_2$; $\text{OH} \cdot \text{C}_6\text{HMePr}(\text{Hg} \cdot \text{OAc})_2 + 2\text{NaCl} = 2\text{CH}_3 \cdot \text{CO}_2\text{Na} + \text{OH} \cdot \text{C}_6\text{HMePr}(\text{HgCl})_2$, and $\text{OH} \cdot \text{C}_6\text{HMePr}(\text{HgCl})_2 + 2\text{I}_2 = 2\text{HgClI} + \text{OH} \cdot \text{C}_6\text{HI}_2\text{MePr}$. Merck's compound also undergoes these changes and differs from that obtained by the author in that it is contaminated with free thymol.

Phenol yields a similar compound, from which a di-iodophenol may be obtained. On the other hand, β -naphthol and vanillin, although they react promptly with a cold saturated solution of mercuric acetate in acetic acid, give only mono-substituted products, from which, by way of the chloro-compounds, an iodonaphthol and an iodovanillin are obtainable.

Diacetatomercurithymol, $\text{OH} \cdot \text{C}_{10}\text{H}_{11}(\text{Hg} \cdot \text{OAc})_2$, prepared from thymol and a saturated solution of mercuric acetate in acetic acid, forms lustrous crystals and its sodium derivative large plates.

Dichloromercurithymol, $\text{OH} \cdot \text{C}_{10}\text{H}_{11}(\text{HgCl})_2$, yields thymol when reduced by means of zinc and potassium hydroxide; the *di-iodo-thymol*, $\text{C}_{10}\text{H}_{11}\text{I}_2 \cdot \text{OH}$, is an almost colourless oil, b. p. $215^\circ/16$ mm. (partial decomp.).

Diacetatomercuriphenol, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{Hg} \cdot \text{OAc})_2$, forms crystals, and *dimercurichlorophenol*, $\text{OH} \cdot \text{C}_6\text{H}_3(\text{HgCl})_2$, yields the di-iodophenol described by Hlasiwetz (*Ber.*, 1869, 2, 524) when treated with a solution of iodine in aqueous potassium iodide.

Acetatomercuri- β -naphthol, $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{Hg} \cdot \text{OAc}$, crystallises in lustrous needles, and, without dissolving or changing in appearance, is converted by aqueous sodium chloride into *chloromercuri- β -naphthol*, $\text{OH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{HgCl}$, which may then be transformed into *1-iodo- β -naphthol* (cf. Meldola, *T.*, 1885, 47, 525).

Acetatomercurivanillin, $\text{C}_8\text{H}_7\text{O}_3 \cdot \text{Hg} \cdot \text{OAc}$, separates in crystals, and *chloromercurivanillin*, $\text{C}_8\text{H}_7\text{O}_3 \cdot \text{HgCl}$, yields the iodovanillin obtained by Carles (*Ber.*, 1874, 7, 616) from vanillin and alcoholic iodine solution.

T. H. P.

Physiological Chemistry.

The Regulation of the Reaction of the Blood. C. L. EVANS (*J. Physiol.*, 1921, 55, 159—192; from *Physiol. Abstr.*, 1921, 6, 424).—The buffering of separated plasma (primary buffering) is contrasted with that induced in the true plasma of whole blood through the agency of the red corpuscles (secondary). The reaction of plasma, although dependent on the ratio of free to fixed carbon dioxide, is not wholly determined by this, but also by the other salts present, which lower the reaction by P_H 0.3. The effect of plasma proteins as buffers is negligible in practice. A slight modification of the Hasselbalch formula, with the use of values for $P \cdot K_1$ derived from observations made on plasma, allows of the calculation of the reaction of a plasma from the usual data. The carbon dioxide reaction curves for plasmata of varying bicarbonate content are parallel, whilst the P_H at a given carbon dioxide pressure varies directly as the logarithm of the bicarbonate content as for bicarbonate solutions; these relations are much less accurately maintained when whole blood is dealt with, first, because of differences in the extent and range of secondary buffering; secondly, because of capricious post-mortem changes in the corpuscles. Blood of high haemoglobin or of low bicarbonate content has a flatter carbon dioxide reaction curve than that in which either or both of these proportions is reversed. When a blood shows a reduction of carbon dioxide capacity on keeping, this change affects the corpuscles more than the true plasma, which tends to maintain a constant bicarbonate content at a given carbon dioxide pressure; this is yet another instance of the operation of secondary buffering in all circumstances which otherwise would tend to lower the P_H of the blood (plasma). Plasma, blood, and bicarbonate solutions alike are more alkaline at higher than at lower temperatures. E. S.

Regulation of the Alkalinity of the Blood. J. B. S. HALDANE (*J. Physiol.*, 1921, 55, 265—275; from *Physiol. Abstr.*, 1921, 6, 424—425).—Ingestion of 5 to 55 grams of ammonium chloride in man causes a fall in the alveolar carbon dioxide and in the blood carbon dioxide capacity, and a rise in the acid, ammonia, and phosphate of the urine. The depression of the alveolar carbon dioxide is roughly proportional to the rate of excretion of acid plus ammonia. The ratio of acid to ammonia depends on the amount of phosphate available for excretion, and this amount falls as the acidosis progresses. The various effects are probably due to conversion of part of the ammonium chloride into urica, thus freeing the hydrochloric acid. E. S.

Physico-Chemical State of Sugar in the Blood. K. ONOHARA (*Brit. J. Expt. Path.*, 1921, 2, 194—196; from *Physiol. Abstr.*, 1921, 6, 440—441).—As shown by Kozawa, dextrose causes swelling of

human red corpuscles. Practically the same hematocrite results, however, were obtained with human red corpuscles treated with the serum of a diabetic patient, normal serum with the addition of isotonic dextrose solution, or isotonic dextrose-saline solution. It may therefore be assumed that sugar in the circulating blood is present in the same physico-chemical character as in the solution of free dextrose, that is, it is present as free sugar. E. S.

The Dextrose Content of Arterial and Venous Blood from Muscle. R. EGE and V. HENRIQUES (*Compt. rend. Soc. Biol.*, 1921, 85, 610—611; from *Physiol. Abstr.*, 1921, 6, 441).—The experiments were conducted on the hind-limb of the goat and dog after preparation of the animals by fasting and administration of phloridzin to remove all stores of carbohydrate. Under these conditions, the arterial blood-sugar was 0.004%, while the venous blood-sugar was one-fifth of this, namely, 0.0008%. E. S.

Coagulation of the Blood. II. The Clotting Complex. H. W. C. VINES (*J. Physiol.*, 1921, 55, 287—295; from *Physiol. Abstr.*, 1921, 6, 424).—The clotting complex (cf. this vol., i, 525) is a combination of a lipid, calcium, and a protein. The calcium-lipoid combination is essential, and does not yield calcium ions; the function of the protein, which seems to render the lipid compound more sensitive and may act by keeping it in a state of fine suspension, is apparently secondary. The compound has properties resembling those of the thrombokinas of Morawitz rather than of the prothrombin of Howell. The anti-coagulants (oxalates, citrates, fluorides, hirudin, and cobra venom) act as antikinase; hirudin acts also as an antithrombin. E. S.

The Chloride Content of the Serum of Sucklings. K. SCHEER (*Jahrb. Kinderheilk.*, 1921, 94/44, 295—314; from *Physiol. Abstr.*, 1921, 6, 426).—The chloride content of the serum of sucklings is fairly constant, and about 0.50 to 0.59%. At the beginning of digestion, the chloride decreases quickly, and regains its former level afterwards. This connexion between the serum chloride and the secretion of gastric juice is quite independent of the kind of food. Infusion of isotonic dextrose solution effects a diminution of the serum chlorides of some hours' duration. E. S.

A Method for Investigating the Hæmolytic Activity of Chemical Substances. ERIC FOXNER (*Proc. Roy. Soc.*, 1921, [B], 92, 285—295).—A new technique is described. Estimations of the hæmolytic activity of a number of substances indicate that, for a constant quantity of hæmolytic substance, the relation between temperature and time of hæmolysis is expressed by a hyperbola. E. S.

The Calcium Content of Egg-white. HANS KREIS and JOSEF STUDINGER (*Schweiz. Apoth. Zeit.*, 1921, 59, 193—196).—White of fresh hens' eggs yields 0.75—0.80% of ash containing 0.59—4.25% of calcium oxide; the lime content of the ash of egg-yolk is 11.54—12.32%. When preserved in calcium hydroxide solution, VOL. CXX. i.

lime is not absorbed, so that estimations of calcium in the ash of the albumin give no indication of such preservation (cf. Rőzenyi, *Chem. Zeit.*, 1904, 28, 620).
CHEMICAL ABSTRACTS.

Composition of the Egg of the Brown Frog (*Rana fusca*) at the Time of Laying. E. F. TERROINE and H. BARTHÉLÉMY (*Compt. rend.*, 1921, 173, 611—613).—The composition of the ovarian eggs of the brown frog at the time of laying is remarkably constant and is independent of the age, weight, etc., of the individual females. The organic matter of the egg is almost entirely composed of nitrogenous substances, fats, and lipoids. There is a remarkable similarity in composition between the eggs of the frog and those of the trout and silk-worms.
W. G.

Is Glycogen the Source of the Acids developed in Autolysis? W. MORSE (*Proc. Soc. Expt. Biol. Med.*, 1921, 18, 246—247; from *Physiol. Abstr.*, 1921, 6, 406).—Ox liver was used for the experiments on autolysis. The results indicate that glycogen may be one of the precursors of substances concerned with the development of acidity.
E. S.

Internal Secretion of the Spleen. N. B. EDDY (*Endocrin.*, 1921, 5, 461—475; from *Physiol. Abstr.*, 1921, 6, 448).—It is claimed that the spleen produces an internal secretion which regulates the number of red corpuscles in the blood-stream. This is supported by the changes in the erythrocytes after splenectomy; the modification of the blood-picture in hyperplasia of the spleen, ameliorated in some cases by splenectomy, and the specific effects on the red corpuscles of injection of splenic extract. It is suggested that the chief function of the spleen is the removal from the circulation of the disintegrated erythrocytes; that the splenic cells elaborate this material, producing thereby an internal secretion, which was a component of the erythrocyte, either stroma or pigment portion; that this internal secretion reduces the resistance of all the red blood-corpuscles, the effect amounting to actual destruction of the older cells, and, finally, that this internal secretion, possibly after modification by the liver, stimulates the erythrogenic function of the bone-marrow, and is used up in the manufacture of new corpuscles.
E. S.

Creatinine and Creatine in Muscle Extracts. I. A Comparison of the Picric Acid and the Tungstic Acid Methods of Deproteinisation. II. The Influence of the Reaction of the Medium on the Creatinine-Creatine Balance in Incubated Extracts of Muscle Tissue of the Albino Rat. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1921, 48, 127—131 and 133—141).—The author describes procedures whereby concordant results in the estimation of creatinine in muscle extracts may be obtained by the use of either picric acid or tungstic acid as protein precipitants. Using the picric acid method, he finds that, if extracts of the muscle tissue of the rat are incubated at body temperature, the creatinine increases at the expense of the creatine. This change is influenced by the reaction of the medium, the optimum effect

being obtained when this is buffered to neutrality by a phosphate mixture. The presence of an enzyme capable of bringing about this change is suggested but not proved (cf. Hahn and Barkan, this vol., i, 515).
C. R. H.

Action of various Lactones on Worm Muscles. LUDWIG LAUTENSCHLÄGER (*Ber. deut. Pharm. Ges.*, 1921, 31, 279—291).—Further experimental support is adduced of Trendelenburg's theory (*Arch. Expt. Path. Pharm.*, 1915, 79, 190) that the anthelmintic action of santonin and similarly constituted compounds is to be ascribed to the lactone structure, and comparative experiments have shown further that the lactone group must be associated with a carbon ring system, open-chain lactones having no anthelmintic action. The naphthalene nucleus in santonin can be replaced by a simpler cyclic system, so, for example, phthalide and meconin (dimethoxyphthalide) are as powerful in their action as santonin, and the replacement of one of the methylene hydrogen atoms by a simple alkyl group still further increases their activity. On the other hand, substitution by an aromatic group produces a decided weakening in the anthelmintic action.
G. F. M.

Distribution of Sodium Salts in Plant and Animal Cells. S. FUNCOKA (*Kyoto Igaku Zasshi*, 1918, 15, 85—120).—Sodium may be detected by precipitation as a double sulphate with cerium, or as a triple magnesium and uranyl acetate; a negative result does not exclude the presence of sodium. By these and other reactions, sodium was found in the blood plasma of both vertebrates and invertebrates, but not in their erythrocytes. It was present in the lymph of muscles but not in their fibres. Sodium occurred in the ground substance of cartilage but not in the cells themselves. In other tissues, it was detected in the intercellular substance but not in the cells. In plants, sodium was found in the cell plasma, but not in the nucleus or the chlorophyll bodies.

CHEMICAL ABSTRACTS.

The Variation in the Zinc Content of the Rabbit's Body during Growth. GABRIEL BERTRAND and R. VLADESCO (*Bull. Soc. chim.*, 1921, [iv], 29, 915—917).—In the case of the rabbit, the percentage of zinc present in the whole body shows a maximum at the moment of birth, diminishing gradually during the time of suckling, and then rising rapidly after weaning.
W. G.

The Distribution of Zinc in the Organism of the Fish. M. BODANSKY (*Compt. rend.*, 1921, 173, 790—792; cf. this vol., i, 78).—In the red snapper fish, *Lutjanus aya*, the liver and the spleen are the most important centres of accumulation of zinc, and the skeletal portions as well as the branchial arcs, the skin and the fins, contain relatively more zinc than the other tissues such as the muscles. In the catfish, *Ailurichthys marinus*, the branchial arcs and the skeleton have the highest zinc content, followed by the liver, the fins, and the skin, whilst again the muscles contain but little zinc.
W. G.

Calcium in the Blood in Diseases of the Skin. W. C. THRO and MARIE EHN (*Proc. Soc. Expt. Biol. Med.*, 1920, **17**, 115-118, and *ibid.*, 1921, **18**, 189-191).—Gravimetric methods for the estimation of calcium in the blood were vitiated by the presence of calcium in filter-paper; Halverson and Bergeim's volumetric method was therefore subsequently employed. The blood plasma of normal persons contained from 7.8 to 9.8 mg. of calcium per 100 c.c. The average amount of calcium present was low in cases of furunculosis, diabetes, hemophilia, and puerpura hemorrhagica, normal in cases of hemiplegia, secondary anaemia, pneumonia, and familial paralysis, and high in cases of acne, healed pulmonary tuberculosis, and some cases of nephritis. CHEMICAL ABSTRACTS.

- **Chemotherapeutic Experiments with "Bayer 205," a New Trypanocidal Agent of Special Activity.** L. HAENDEL and K. W. JOETTEN (*Berl. Klin. Woch.*, 1920, **57**, ii, 821-823).—0.5 Mg. of the agent causes the permanent disappearance of *Trypanosoma brucei* from mice, for which the lethal dose is 20 mg. Remarkable cures are also effected in the case of the dourine disease of horses. Some trypanosomes are not eliminated, for example, *T. lewisii*. Cf. the two following abstracts. G. B.

Experiments with a New Trypanocidal Agent ("Bayer 205") on Trypanosomes Pathogenic to Man and to Animals. MARTIN MAYER and HEINZ ZEISS (*Arch. Schiffs- u. Tropenhygiene*, 1920, **24**, 257-294; cf. preceding abstract).—The curative subcutaneous dose for mice is 0.06 mg., the lethal dose 10 mg. The substance is an unfailing therapeutic agent for mice, rats, guinea-pigs, and rabbits infected with *T. brucei* (Nagana), *T. equiperdum*, *T. equinum*, *T. gambiense* (human sleeping sickness), and *T. rhodesiense*. Smaller doses have a prolonged prophylactic effect.

G. B.

Action of "Bayer 205" on *Trypanosoma equiperdum* in Experimentally Infected Mice. C. M. WENYON (*Brit. Med. J.*, 1921, ii, 746; cf. preceding abstract).—0.005 Gram per kilo given intravenously frees mice from *T. equiperdum* in the course of forty-eight hours.

G. B.

Action of Bismuth on Syphilis and on Nagana trypanosomiasis. Treatment of Syphilis by Bismuth. R. SAZERAC and C. LEVADITI (*Compt. rend.*, 1921, **172**, 1391; **173**, 338).—Sodium bismuth tartrate, suspended in oil, has a very favourable effect on syphilis in rabbits and in man; it is much less effective on Nagana.

G. B.

Treatment of Syphilis by Bismuth. LOUIS FOURNIER and L. GUENOT (*Compt. rend.*, 1921, **173**, 674-676).—Results obtained with human syphilis amply confirm the conclusions of the preceding abstract; bismuth is a most promising agent.

G. B.

The Fate of Salicylic Acid and some of its Derivatives in the Organism. W. DEVRIENT (*Arch. expt. Path. Pharm.*, 1921, 90, 242—255; from *Physiol. Abstr.*, 1921, 6, 439).—Not more than 15% of the salicylic acid administered is excreted in the urine. Sauerland's method of estimating it is found to be exact. E. S.

The Antipyretic Action of some Derivatives of Dimethylphenetidine. HEINRICH RHODE (*Ber. deut. Pharm. Ges.*, 1921, 31, 271—279).—In the dimethylphenetidinc series, as in the phenetidinc series, the acetyl derivative has a much stronger antipyretic action than the other acyl derivatives, but it is nevertheless considerably weaker than phenacetin in its fever-reducing properties. Although phenetidinc is stronger in its action than phenacetin, yet dimethylphenetidinc is weaker than phenacetin, but it is noteworthy that experiments on rabbits free from fever showed a greater reduction in temperature after administration of the former than after an equal dose of the latter. Aryldimethylphenetidines such as the acetylsalicyl- or *p*-aminobenzoyl-derivatives are stronger in their action than formyl- or valeryl-dimethylphenetidinc, but weaker than the acetyl derivative or dimethylphenetidinc itself. Finally, although phenetidinc is a stronger febrifuge than phenacetin, yet ethoxydimethylphenacetin is more powerful than diethoxydimethylphenetidinc. No logical connexion can therefore be traced between the chemical constitution and the physiological action of these phenetidinc derivatives.

G. F. M.

Chemistry of Vegetable Physiology and Agriculture.

Physiology of Methane Bacteria. E. MÜNZ (*Halle Diss.*, 1915, 61 pp.; from *Bied. Zentr.*, 1921, 50, 390).—*Bacterium methanicum* (Söhngen's *Bacillus methanicus*) has minimum 18°, maximum 40°, optimum 34°. The most favourable conditions for its activity are high methane and low oxygen concentration, the optimum oxygen concentration being 2%; light is without influence on the absorption of methane. Under autotrophic conditions, it multiplies and produces organic matter. Although other hydrocarbons and carbon monoxide cannot be substituted for methane, alcohols, carbohydrates, and salts of organic acids giving rise to hydrocarbons may be utilised. Nitrogen is utilised both in inorganic forms (nitrates and ammonium salts) and in organic forms (peptone, leucine, asparagine). The organisms may also live heterotrophically.

G. W. R.

The Micro-organisms Producing Acetone. ALBERT BERTHOLOT and (MILE) E. OSSART (*Compt. rend.*, 1921, 173, 792—794).—In addition to the anærobic organisms used by Fernbach

in the manufacture of acetone, there exist, widely distributed in nature, many other organisms, both aerobic and facultative anaerobes, capable of producing acetone, although to a smaller extent. The amounts of acetone produced by a given organism vary considerably with the nature of the medium.

W. G.

Acclimatisation of Yeast to Ammonium Fluoride and its Reversion in Wort. ELLIS I. FULMER (*J. Physical Chem.*, 1921, 25, 455—472).—The toxicity of aqueous and aqueous alcoholic solutions of ammonium fluoride toward yeast has been investigated. It is shown that alcohol increases the toxicity. In acclimatising yeast to ammonium fluoride it is not necessary to commence with low concentrations (Effront's stepping-up method); the cells may be planted at once in the more concentrated solutions of fluoride and wort and will grow if left long enough. The time elapsing between seeding and active fermentation depends on the method of preparing the wort, on the character of the individual yeast cells, and on the previous history of the culture. Yeasts acclimatised to a given concentration of fluoride by different routes behave differently towards more concentrated fluoride solutions. If the logarithm of the interval between seeding and active fermentation be plotted against concentration, for various yeasts, acclimatised and unacclimatised, the experimental data fall on straight lines radiating from a point corresponding with about 7—8 grams of ammonium fluoride per litre. The highest concentration in which yeast will grow is about 7 grams per litre. Yeast acclimatised to ammonium fluoride is more resistant to phenol than is normal yeast. Acclimatised yeast may be grown on fluoride free wort agar for twelve days or in fluoride-free wort for one hundred and ninety hours without completely reverting to normal. When yeast is planted in wort containing ammonium fluoride, a proportion of the cells die, that is, they will not reproduce on fluoride-free wort agar. The number of living cells decreases, passes through a minimum, which may be less than 1 in 1200 of those originally present, and then increases. Selection plays a part in the acclimatisation. Measurements of the rate of reproduction of yeast in wort with and without ammonium fluoride show that the cells which are not killed outright undergo a period of paralysis, after which they reproduce, giving rise to fluoride resistant cells. Adaptation plays a part in the acclimatisation. The maximum value for the duration of paralysis may be calculated from the experimental results.

J. F. S.

Catalytic Processes of Physiological Importance Effected by Light. KURT NOACK (*Zeitsch. Bot.*, 1920, 12, 273—349).—The chemical action of light on cells occurs through the agency of substances which transform light energy into chemical energy. Two groups of such catalysts are recognised: fluorescent organic compounds, and salts of certain heavy metals. Both serve as carriers of oxygen. From experiments on chromogens and many plants the author concludes that the fluorescent organic compounds

act by the formation of peroxides. Their action is stopped by sodium sulphite. The salts of the heavy metals act by change in the valency of the metal.

CHEMICAL ABSTRACTS.

The Relation of the Hydrogen-ion Concentration of Nutrient Solutions to Growth and Chlorosis of Wheat Plants. A. G. McCALL and J. R. HAAG (*Soil Sci.*, 1921, 12, 69—77).—Wheat plants were grown for two months on sand cultures supplied with four different nutrient solutions, each of which was modified in such a way as to have three distinctly different p_H values without materially altering the solutions with respect to the concentrations of the six essential ions. The results indicate that hydrogen-ion concentration exerted a very marked influence on the rate of growth and was also an important factor in the control of chlorosis. There was some evidence that the plants grown in solutions having p_H values ranging from 4.02 to 7.0 were suffering from the lack of available iron or from faulty metabolism resulting from the immobility of the iron within the plants.

W. G.

The Relation of Sulphates to Plant Growth and Composition. H. G. MILLER (*J. Agric. Res.*, 1921, 22, 101—110).—Nodule production and nitrogen assimilation of legumes were stimulated by the addition of sulphates. On the other hand, the supply of nitrate available to the plant appeared to limit the amount of sulphur assimilated. In the case of rape, no direct relationship between nitrogen and sulphur assimilation was observed. [See also *J. Soc. Chem. Ind.*, 1921, 861A.]

A. G. P.

Vegetable Assimilation and Respiration. XIV. Assimilation by Submerged Plants in Dilute Solutions of Bicarbonates and of Acids: an Improved Bubble-counting Technique. A. J. WILMOTT (*Proc. Roy. Soc.*, 1921, [B], 92, 304—327).—Disturbances in bubbling experiments are eliminated by using a glass bubbler and a bubbling cup. By means of this apparatus it is shown, (1) that the increased rate of bubbling by submerged water plants when placed in acid solution is due to the decomposition of calcium carbonate deposited on their surface, (2) that the rate of assimilation of carbon dioxide from sodium hydrogen carbonate solution corresponds with the calculated concentration of carbon dioxide, the conclusion being drawn that plants do not possess the power of decomposing sodium hydrogen carbonate.

E. S.

First Products of the Chlorophyll Assimilation of Carbon. E. ROUGE (*Schweiz. Apoth. Zeit.*, 1921, 59, 157—161, 175—178).—The history of the problem of carbon dioxide absorption by plants is reviewed. A test for glycollaldehyde consists in the preparation of the *p*-nitrophenylthiazone, reddish-brown needles, m. p. 177° (decomp.), and soluble in alcoholic potassium hydroxide with a blue colour. By this method, glycollaldehyde has been identified in various green leaves; the method of its formation is considered theoretically.

CHEMICAL ABSTRACTS.

Hemicellulases in Resting Seeds and their Supposed Occurrence in Higher Animals. AUGUST RIPPEL (*Landw. Versuchs.-Stat.*, 1921, 97, 179—193).—It has been suggested that the digestion of hemicelluloses by higher animals is due to the occurrence of appropriate enzymes in the alimentary tract. Working with seeds of *Lupinus angustifolius*, L., the author shows that an intensive autolysis of the water-soluble hemicelluloses takes place with formation of sugar; there is also a further autolysis of hemicelluloses which are not immediately soluble in water. The enzyme concerned in the reaction is specific and present as such, is not destroyed by heating at 105°, and is distributed throughout the seed. Similar autolytic actions were observed in the case of *Galium aparine*, L., and *Asparagus officinalis*, L. The occurrence of hemicellulases in seeds is a sufficient explanation of the digestion of hemicelluloses by animals. G. W. R.

Incrustive Substance of Plants. I. Method of Preparing Plant-tissue Substances in the Pure Condition. I. ERICH SCHEIDT and ERICH GRAUMANN (*Ber.*, 1921, 54, [B], 1860—1873).—The complete removal of incrustive substances from plants, for example, lignin from wood, has only been possible previously by the use of reagents which also attack the polysaccharide. It is now shown that unchanged carbohydrates, completely free from incrustive substance, can be readily prepared by the use of aqueous solutions of chlorine dioxide which have no effect on cellulose, mercerised cellulose, oxycellulose, mannan, xylan, starch, and fungus-cellulose. The stability of the carbohydrates towards chlorine dioxide is confirmed further by the observation that their components, dextrose, mannose, galactose, laevulose, xylose, arabinose, maltose, and glucosamine hydrochloride do not react with solutions of the gas. The presence of small amounts of incrustive substance is readily detected by the consumption of chlorine dioxide, and in consequence of this behaviour it is easily possible to estimate quantitatively the percentage of incrustive and tissue substance in portions of plants. In this manner pine (*Pinus silvestris*, L.) is found to contain 63.28% of tissue substance and 36.72% of lignin, whereas Willstätter and Zechmeister found only 27.35% of the latter. The consumption of chlorine dioxide is small amounting, in the case of pine wood, to 13.50% of the weight of the wood.

With the help of chlorine dioxide it has been found possible to establish the presence of polysaccharides in lignin; the hydrolysis of these only becomes possible after the destruction of the components of lignin which are attacked by solutions of the gas.

The preparation of a saturated aqueous solution of chlorine dioxide from potassium chlorate and oxalic acid is described fully, as are also the methods of estimating chlorine dioxide in aqueous solution. The sensitiveness of the carbohydrates or incrustive substance is measured by allowing them to remain in contact with the *N*/20- or *N*/5-solution of the gas for a period of twenty-four hours at the atmospheric temperature (a little acid is added if

necessary to overcome possible alkalinity of the material) and estimation of the concentration of the solution before and after this treatment. For the removal of incrustive substance, the wood shavings are extracted with alcohol-benzene mixture to remove the greater part of the resin, finely ground, and again extracted. The dry wood (100 grams) is covered with *N*/5-chlorine dioxide solution (2-3 litres) in a stoppered, brown glass bottle and allowed to remain in diffused light and with occasional agitation for about twenty-four hours at the atmospheric temperature. The residue is filtered and treated successively with water, 2% aqueous sodium sulphite solution, and hot water, and the processes are repeated until the material is free from incrustive substance (generally three to eight times). The preparation of incrustive-free xylan and mannan is described in detail; in each case, it is noticeable that the action of sodium hydroxide solution causes changes in the respective molecules which lead to the presence of groups attackable by chlorine dioxide. H. W.

Hydrocyanic Acid in Sudan Grass. C. O. SWANSON (*J. Agric. Res.*, 1921, 22, 125-138).—Hydrocyanic acid was obtained from the leaves of Sudan grass by digesting the macerated material with water at room temperature for six hours. The free acid does not occur in the green plant as such, but is produced by the action of enzymes during maceration and also during severe wilting of the plant. [See also *J. Soc. Chem. Ind.*, 1921, Dec.] A. G. P.

Carbohydrates of the Root of the Cat-tail (*Typha latifolia*). ZALIA JENCKS (*Proc. Soc. Expt. Biol. Med.*, 1919, 17, 45-46).—The root of the cat-tail, recently recommended as a valuable food for man, contains 81% of carbohydrates. The most abundant carbohydrate of the root gives a blue colour with iodine, forms a characteristic paste with hot water, is readily digested (in contrast with inulin) by saliva, and yields on hydrolysis a dextrorotatory solution from which an osazone, identical with glucosazone, was prepared. It thus corresponds with starch. The "flour" was found to contain 56.8% of carbohydrate. Mice were fed for a week on otherwise adequate diets containing 30% of the "flour" without any evident untoward results. The animals gained in weight on the ration.

CHEMICAL ABSTRACTS.

The Influence of certain Fertiliser Salts on the Growth and Nitrogen Content of some Legumes. ALEXANDER MAC-TAGGART (*Soil Sci.*, 1921, 11, 435-455).—Nitrogen was applied in the form of dried blood, phosphorus as disodium hydrogen phosphate, potassium as potassium chloride, and sulphur as calcium sulphate, and all the soils received a dressing of calcium carbonate. The fertilisers were applied singly and in groups, and the crops were lucerne, Canadian field peas, and soja beans. Of all the four fertiliser elements phosphorus showed the most marked effect whether applied singly or with other fertilisers. It increased the dry matter, total nitrogen, and, to a lesser extent, the percentage of nitrogen

in all three legumes. Nitrogen had very little, if any, beneficial effect on the legumes. The action of potassium was not uniform on the three crops examined. Sulphur, in the form of gypsum, benefited to some extent the lucerne crop, but had no effect on the peas or beans. There appeared to be some correlation between the plant dry matter produced and subsequent soil nitrification.

W. G.

The Effect of Soil Temperature on the Development of Nodules on the Roots of certain Legumes. F. R. JONES (*J. Agric. Res.*, 1921, 22, 17—31).—Maximum nodule production occurs at about 24° in all plants examined, and is in no way connected with maximum growth of the plant. Usually conditions favourable to nodule production bring about high nitrogen content in the foliage.

A. G. P.

Influence of Temperature on the Absorbent Properties of Soils. STOQUER (*Compt. rend.*, 1921, 173, 731—733).—Four types of soils were used, 100 grams of the soil being shaken with 250 c.c. of ammonium sulphate solution at the given temperature for one hour, and the ammonia remaining in the solution estimated by distillation. The temperatures used were 0°, 16°, 35°, and 55°. In all cases, the absorption diminished as the temperature increased, and with two types of soil there was a negative absorption when a 0.002% solution of ammonium sulphate was used at temperatures above 0°.

W. G.

Concentration and Composition of the Soil Solution. F. W. PARKER (*Soil Sci.*, 1921, 12, 209—232).—The author discusses the different methods which have been used for obtaining the soil solution in an unaltered state. A description is given of a displacement method in which ethyl alcohol is used as the displacing liquid. The constancy of composition of the displaced solution was checked by freezing-point determinations which also served to indicate the appearance of the displacing liquid in the percolate. The concentration of the soil solution was found to be inversely proportional to the amount of moisture originally present in the soil. A study of the freezing points of soils containing varying amounts of moisture showed that the depression gives no measure of the concentration of the soil solution at ordinary moisture contents. In soils nearly saturated with water, freezing-point depressions may give some indication as to the concentration of the soil solution. The discrepancies at low moisture contents are due to the fact that the water is present in the form of capillary films, and not to its removal from the rôle of solvent, as has been assumed by other workers.

G. W. R.

Effect of Salt Solutions on the Soil. O. NOLTE (*Landw. Versuchs.-Stat.*, 1921, 98, 135—153).—A continuation of earlier work (A., 1917, i, 621) on the reaction between the soil and salt solutions. The reaction of a soluble salt with soil is reflected in its

effect on the permeability. Neutral salts and hydrogen ions favour flocculation whilst hydroxyl ions favour deflocculation. The effect of any salt on soil structure is thus determined by its reaction with the soil constituents. The effect of different solutions on soil structure was studied in a special apparatus, whereby the rate of percolation through a soil column could be followed over long periods. The continued passage of distilled water leads to a steady decrease in permeability consequent on the washing out of soluble salts. The effect of each solution was studied by allowing it to percolate for three weeks after a preliminary period of three to four weeks in which distilled water was passed through. The percolating liquid was collected daily and analysed weekly as a composite sample. The results are set out in graphic form and should be consulted in the original paper. They are in general agreement with theoretical considerations.

G. W. R.

The Reaction of Potassium Ammonium Nitrate with Soil. NIKOLAUS KEMPF (*Landw. Versuchs.-Stat.*, 1921, 97, 195—217).—The absorption of the ions of salts by the soil was studied, using potassium ammonium nitrate (Kaliammoniaksalpeter), a new fertiliser prepared from synthetic ammonium nitrate and "40% potash salt."¹⁷ As a preliminary experiment, a sample of the soil under experiment was extracted with water in order to discover its content in soluble salts which might be presumed to take part in absorption equilibria. Known weights of the soil were uniformly moistened with known volumes of a solution of the fertiliser and after remaining for varying times the soil solution was obtained by adding excess of water and filtering. The amount of absorption of each ion was determined by estimating the amount in solution and subtracting from the amount added, making allowance for the water soluble material originally present in the soil. The univalent ions, potassium, sodium, and ammonium are all absorbed to some extent by the soil and approximately equivalent amounts of the bivalent ions, calcium and magnesium are displaced. While the amount of absorption of sodium decreases, the absorption of potassium and ammonium increases with time. The approximate equivalence of the univalent ions absorbed with the bivalent ions displaced into solution holds throughout. A small absorption of nitrate takes place. The absorption of chloride lies within the limits of experimental error. The behaviour of the sulphate ion is irregular and the amount in solution decreases after long keeping, probably owing to the formation of calcium sulphate. Absorption is almost instantaneous, and the further changes above described take place slowly.

G. W. R.

Solubility of Anions in Alkali Soils. W. P. KELLEY and S. M. BROWN (*Soil Sci.*, 1921, 12, 261—285).—The absorption of salts by alkali soils has been studied by determining the amount of different anions extracted by water under varying conditions of time of shaking, and ratio of water to soil. Experiments were also made in which soils were extracted with successive portions

of water. Whilst the amount of total solids extracted increases with time of shaking, no consistent variation was found in the case of any of the anions, and it is concluded that approximate equilibrium is attained at the end of one hour. Variation in the ratio of water to soil was without effect on the amount of chloride and nitrate extracted. In the case of carbonate and hydrogen carbonate, however, two of the three soils studied gave up increasing amounts with larger volumes of extracting water. A slight increase in the amount of sulphate extracted was also observed with increase of the ratio of water to soil. In the case of chloride, nitrate, and sulphate, a very large proportion of the total amount was extracted by the first treatment with water; in the case of the normal and hydrogen carbonate, however, greater amounts were dissolved by the second extraction. The conclusion is drawn that alkaline salts are either adsorbed or held in loose combination to a greater degree than neutral salts.

G. W. R.

The Effect of Organic Matter on Soil Reaction. R. E. STEPHENSON (*Soil Sci.*, 1921, 12, 145—162).—A study is made of the effect of ploughing in crop residues, etc., on the soil reaction. In general, the lime requirement of the soil (Tacke method) is reduced by this treatment until nitrification begins. Determinations of the H-ion concentration show that true acidity also is decreased. Highly organic and clay soils show a marked capacity for buffering, a property which is considerably limited in sands. Sulphuric acid and physiologically acid salts tend to raise the H-ion concentration, but citric acid does not. Ammonium sulphate causes a greater increase in acidity than does its nitrogen equivalent in albumin; but less than the equivalent in mixed nitric and sulphuric acids. A value of $p_H=8$ seems to be about the limit of alkalinity produced by limestone. [See also *J. Soc. Chem. Ind.*, 1921, 860A.] A. G. P.

Soil Acidity and Bacterial Activity. R. E. STEPHENSON (*Soil Sci.*, 1921, 12, 79—132).—The work described is a continuation of that in a former paper [*ibid.*, 1918, 6, 413—439], and deals with the effects on soil reaction and bacterial activity in soils of various organic nitrogenous manures, both in the presence and absence of lime. The lime requirement was in no case increased by organic treatment, except during the rapid production of nitrates. Lime stimulates nitrification, whereas ammonification was greater in unlimed soils. The latter is due to the lower activity of nitrifying organisms in this case. The total ammonia plus nitrates is greater in unlimed than in limed soil treated with organic material. Dung and timothy hay reduced ammonification and nitrification below that of untreated soil. Green manures were more rapidly attacked than dried material.

In practically all cases unlimed soils had a greater non-protein nitrogen content than the limed. Generally speaking, the essential soil organisms are active in soils of at least moderate acidity.

A. G. P.

General and Physical Chemistry.

Refractive Indices of Mercury and Thallium Vapours.
 J. C. McLENNAN (*Proc. Roy. Soc.*, 1921, [A], 100, 191–200).—The refractive indices of mercury and thallium vapour have been determined for a number of wave-lengths both by the prism method and the interferometer method. A method is described by which interferometer tubes and hollow prisms of clear fused quartz, free from distortion and all trace of devitrification, can be made. These instruments were employed in the present experiments and found to yield satisfactory results. The dispersion curve for non-luminous thallium vapour indicates the existence of anomalous dispersion at the wave-lengths $\lambda\lambda$ 5350.65 and 6000 Å.U. The following values of the refractive index were obtained: mercury vapour at normal pressure and temperature by the interferometer method, λ 4860, μ_0 1.000949; λ 5132, μ_0 1.000943; λ 6110, μ_0 1.000924; λ 6230, μ_0 1.000882; prism method, λ 4358.56, μ_0 1.000942; λ 5460.97, μ_0 1.000902; λ 5780, μ_0 1.000891; λ 6234.31, μ_0 1.000890; thallium vapour at 540°, λ 4358.56; μ 1.000229, λ 4861.49, μ 1.000110; λ 5460.97, μ 1.000293; λ 5769.45, μ 1.000222; λ 5790.49, μ 1.000144; λ 5893, 1.000165; λ 6234.31, μ 1.000309; λ 6563.04, μ 1.000142.
 J. F. S.

Hydrogen Spectra from Long Vacuum Tubes. R. W. WOOD (*Phil. Mag.*, 1921, [vi], 42, 729–745; cf. A., 1920, ii, 569).—A continuation of previous work (*loc. cit.*). It is shown that in a tube of great length (190 cm.), containing hydrogen with a suitable trace of water-vapour, the centre of the tube exhibits the Balmer series with the secondary spectrum reduced to 1/50 of its usual intensity. The ends of the tube (to a distance of about 40 cm. from the electrode bulbs) show the secondary spectrum strongly developed in addition to the Balmer series. The phenomena are of the same nature with a continuous current of high potential as with an alternating current; that is, the secondary spectrum develops at both the anode and cathode. With the tube in this condition, the central portion shows a bright flash of the secondary spectrum on closing the switch; the duration of this flash is about 1/50 sec.; on opening the switch the gas recovers its initial condition in about 1/5 sec. and shows the flash again on closing the switch. The secondary spectrum is attributed to molecular hydrogen by Merton, Stark, and others. The first rush of the current appears to break down the molecular hydrogen with the emission of a flash, leaving only atomic hydrogen in the centre of the tube (which gives the Balmer lines). On stopping the current, molecular hydrogen is reformed in about 1/5 sec. The breakdown, however, requires the presence of a trace of water-vapour. A very weak current produces a fairly strong secondary spectrum in the centre

of the tube with the Balmer lines weak or absent. Increase of current weakens the secondary spectrum, which passes through a minimum of intensity as the current becomes stronger and at the same time the Balmer lines increase in intensity. This is probably explained by the fact that molecular hydrogen is reformed as rapidly as it is broken down by a weak current. As the current strength increases the proportion of atomic hydrogen becomes greater with weakening of the secondary spectrum and augmentation of the Balmer lines. This, however, does not go on indefinitely, for with a further increase of current beyond a definite value both spectra increase in intensity at about the same rate. In any case, the percentage of molecular hydrogen cannot be reduced below a certain minimum value. With dry hydrogen and the tube thoroughly free from water-vapour, the Balmer lines disappear entirely from the entire tube (with the exception of a faint trace of H_α). In this stage, a strong group of lines appears in the ultra-violet between the 4th and 5th Balmer lines. When the tube is in this, the white stage, operation with condenser discharges gives a red discharge which shows strongly developed Balmer lines, indicating that momentary currents of several thousand amperes are able to break up molecular hydrogen even in the absence of water-vapour.

J. F. S.

Structure of the Balmer Series Lines of Hydrogen. J. C. McLENNAN and P. LOWE (*Proc. Roy. Soc.*, 1921, [A], 100, 217–226).—The structure of the Balmer series of hydrogen lines has been examined, using a long discharge tube of the type recently introduced by Wood (A., 1920, ii, 569). The following doublet separations were found for the first four members of the Balmer series, $H_4=0.154$ Å.U., $H_3=0.085$ Å.U., $H_2=0.062$ Å.U., and $H_1=0.049$ Å.U. When these separations are plotted against the squares of the corresponding wave-lengths they are shown to lie on a curve which points to the vanishing of the doublet separation at the short wave-length limit of the Balmer series. The lines H_2 , H_3 , H_4 , and H_5 have been shown to consist of triplets when the electric discharge takes place in hydrogen containing a trace of nitrogen. Experiments made to decide whether the third members of the triplets had their origin in the radiations emitted by nitrogen atoms or in a modification produced by the nitrogen in the radiations emitted by the atoms of hydrogen were not decisive.

J. F. S.

The Balmer Series of Hydrogen, and the Quantum Theory of Line Spectra. RAYMOND T. BIRGE (*Physical Rev.*, 1921, 47, 589–607).—To make as accurate a comparison as possible between the best experimental results for the Balmer series of hydrogen and the theoretical results to be expected according to the latest developments of the quantum theory of line spectra, the experimental data are reviewed and the quantum theory of line spectra, as applied to the Balmer series, is summarised historically. The fine structure of H_α ($\lambda=6563\text{Å}$) consists of six lines, two of which

are relatively intense, and the author shows that Merton's measurements (A., 1920, ii, 457) of the separation, half-width and relative intensities of the H_α and H_β doublets accord with values derived from the recent Bohr-Kramers developments of the quantum theory, if a general field of 100 volts per cm. is assumed. A discussion of spectral formulæ for the Balmer series indicates (1) that the Rydberg number is not constant for different lines, (2) that this discrepancy between observed and computed results is somewhat reduced by the application of relativity mechanics, and (3) that the discrepancy is obliterated when account is taken of the fine structure of the lines. The Rydberg constant for hydrogen is then calculated to be $106,977.7 \pm 0.2$ and the Rydberg spectral series constant for a nucleus of infinite mass is computed to be $109,736 \pm 0.2$. A discussion of observations in mixtures of hydrogen and helium made by Merton and Nicholson (A., 1920, ii, 69) at relatively high pressures concludes the paper. The well known neutral effect of helium on neighbouring electrons together with the Maxwellian distribution of velocities, separations, etc., is quite sufficient to account for the experimental results thus far obtained.

CHEMICAL ABSTRACTS.

Temperature and Band Spectra. W. STEUBING (*Physikal. Zeitsch.*, 1921, 22, 507—511).—The band spectrum of iodine vapour has been examined in the positive column of a discharge tube at a series of temperatures. The light of the positive column presents at ordinary external temperatures a yellowish-green colour, but as the temperature is raised this passes into a bluish-violet colour. Spectroscopically, it is found that as the temperature is raised the band spectrum diminishes in intensity, at first in the green and then gradually right across the spectrum to the orange, which is observed at 450° , the limit of the experiment. At the same time, the intensity of the continuous spectrum increases, so that it becomes responsible for the bluish-violet colour of the positive column. The loss of intensity of the band spectrum is accompanied by the appearance of a number of lines which become more intensive the more the spectrum loses its characteristic band appearance.

J. F. S.

Spectrum of Ionised Potassium. J. C. McLENNAN (*Proc. Roy. Soc.*, 1921, [A], 100, 182—190).—The author has photographed the "ground spectrum" of potassium, using electrodeless tubes in which to excite the vapour. The wave-lengths obtained contain the values of 150 lines which were not found by Schillinger (A., 1910, ii, 369), for which an accuracy of 0.5 Å.U. is claimed. In photographing the spectrum with a vacuum spectrograph, wave-lengths were recorded at $\lambda\lambda$ 1742.2, 1493.4, 1395.4, 1199.7, 1135.0, and 1085.3 Å.U.; of these the first may possibly belong to potassium. The remaining five were also found in the helium spectrum, and may be due to atoms of mercury from diffusion from the pump. The wave-lengths of the enhanced spectrum of potassium, from the point of view of numbers and intensity, fall roughly into two divisions

with a certain amount of overlapping. In one division, the "optical" or "spectral" centre of gravity is approximately at $\lambda=3800$ Å.U., and in the other it is in the neighbourhood of $\lambda=2100$ Å.U. This suggests a similarity with the ordinary and enhanced spectra of argon, the one with its centre of gravity at 3800 Å.U. corresponding with the red spectrum of argon, and the other to the blue spectrum of this element.

J. F. S.

The Electrodeless Discharge in Sodium Vapour. JOHN K. ROBERTSON (*Nature*, 1921, **107**, 269).—A brilliant electrodeless discharge is obtained at a temperature of about 300° when a primary Tesla coil is placed about a highly exhausted pyrex bulb containing metallic sodium, and the whole enclosed in an oven. In addition to the *D*-lines, doublets at 6162 (and 6158), 5688 (and 5683), 4667, and 4497 may be observed, as well as faint probable doublets at 5153, 4980, and 4572.

A. F. E.

Emission and Adsorption Spectra of Mercury. J. C. MCLENNAN and W. W. SHAVER (*Proc. Roy. Soc.*, 1921, [A], **100**, 200—217).—Using plates stained with decyanin, the spectra of a number of elements have been photographed in the infra-red region. In the case of mercury, the spectrum was photographed up to $\lambda 11137$ Å.U. By the photographic method, as well as by the use of thalofide cells, it has been shown that non-luminous mercury vapour does not absorb radiation of the wave-length $\lambda 10140$ Å.U. It has been found that slight and scarcely visible deposits of mercury vapour markedly absorb radiation of the wave-length $\lambda=10140$ Å.U., and this result may possibly afford an explanation of the observations made by Dearle (*A.*, 1916, ii, 590; 1919, ii, 126). By the use of thalofide cells (Case, *Physical Rev.*, 1920, 289) and low-intensity mercury arcs, it has been shown that radiation of the wave-length $\lambda=10140$ Å.U. may be strongly absorbed by luminous mercury vapour. From the absence of absorption of radiation of wave-length $\lambda 10140$ Å.U. by non-luminous mercury vapour, it follows that the atoms of mercury in their ordinary state do not possess a resonance potential of 1.26 volts, corresponding with $\lambda 10140$ Å.U., in addition to the well-established one of 4.9 volts, corresponding with $\lambda 2536.72$ Å.U.

J. F. S.

Revision of Series in the Arc Spectrum of Mercury. HERBERT DINGLE (*Proc. Roy. Soc.*, 1921, [A], **100**, 167—181).—The arc spectrum of mercury has been reinvestigated and the lines have been grouped in principal, sharp, diffuse, and fundamental series of quadruplets, a singlet series, and combination lines. Photographs and diagrams of the spectrum are included in the paper. The measurements were all made with a quartz Littrow spectrograph giving a dispersion of 7.9 Å.U. per mm. at $\lambda 2400$ and 12.9 Å.U. at $\lambda 2800$ and the values, given in the international scale, are claimed to be accurate to 0.03 Å.U. or less.

J. F. S.

Anomalous Zeeman Effect and Series System for Neon and Mercury. A. LANDÉ (*Physikal. Zeitsch.*, 1921, 22, 417—422).—The results of the quantum theoretical analysis of the terms of the Zeeman lines are collected and put forward as spectral combination, polarisation, and intensity rules. The complete series systems of neon and mercury are arranged by means of a principle of selection, of the nature of Sommerfeld's conception of the complete doublets and triplets, and from the arrangement, by means of the rules devised from previous work, the Zeeman type of each series is obtained. The agreement with experimental results as to the number, position, and intensity of the Zeeman components confirms the relationship, between the type separated by a magnetic field and the multiplication of lines without a field, which has been previously deduced on the basis of the quantum hypothesis.

J. F. S.

The Electronic Structure of the Heavy Atoms and of their Spectral Lines. A. DAUVILLER (*Compt. rend.*, 1921, 173, 647—649).—The method used in the detailed study of the *L*-series of uranium (cf. this vol., ii, 532) has been extended to gold, platinum, iridium, osmium, and tungsten. The variations of certain homologous rays have been followed and six new rays have been isolated. The wave-lengths of the *L*-rays of the elements tungsten to uranium are tabulated.

W. G.

The Normal Orbit of the Electron in the Atom of Mercury. A. TEREININ (*Nature*, 1921, 107, 203).—A photographic method of examining absorption by non-luminous mercury vapour up to $\lambda 11300$ Å.U. revealed the absence of a marked absorption at $\lambda 10140$, although the pressure of mercury vapour reached one atmosphere. Thus the postulation by Dearle of a second normal orbit in the mercury atom, of which the corresponding ionisation and resonance potentials have never been observed, is unnecessary.

A. A. E.

Absorption of Light by Electrically Luminescent Mercury Vapour. E. P. METCALFE and B. VENKATESACHAR (*Proc. Roy. Soc.*, 1921, [A], 100, 149—166).—Experiments are described in which mercury vapour at low pressures, rendered luminous by the passage of small electric currents, is found to exert powerful selective absorption. It is found that, of the series lines, those belonging to the first and second subordinate series of triplets exhibit heavy absorption. The following lines are absorbed: $\lambda\lambda$ 5461, 4359, 4047, 3542, (3663, 3132, 2967), 5289, 5295, 5308, 3655, 3650, 3126 Å.U. Photometric observations are recorded on the absorption and emission of $\lambda 5461$ Å.U. by columns of mercury-vapour of different lengths and carrying different currents. The relation between the ratio (emission/absorption) and the current density is found to be linear. The applicability of the Stewart-Kirchhoff law to bright line radiation is discussed, and it is shown

that the complexity of a line may have a great influence on its absorption. The lines 5461 Å.U. and 4359 Å.U. have been reversed, so as to appear as dark lines on the white light spectrum of a carbon arc and the sun. The reversal of 5461 Å.U. has been studied in detail with a Fabry and Perot étalon and with an échelon spectroscope.

J. F. S.

Permanganate Absorption Spectrum : Claim for Priority : Formula for Calculating the Uranium Spectrum. JAMES MOIR (*Trans. Roy. Soc. Sth. Africa*, 1921, **10**, 33—34).—The author claims priority for a formula giving the wave-lengths of the bands of permanganates (A., 1920, ii, 573) over Adinolfi (A., 1920, ii, 721). The formulæ put forward by the two authors differ in form, but reduce to the same expression. From the formula for the absorption spectrum of uranyl salts, $n=1/\lambda=2113+66N$, where $N=0, 1, 2, 3$, or 4 (*loc. cit.*), it is now shown that the bands of non-ionised solid salts may be calculated. Thus the bands of autunite are given by dividing the figures calculated by the above formula by the sixth root of the ratio of the molecular weight of the salt to that of UO_2^{+4} . In this case the observed bands are $\lambda\lambda$ 1945, 2000, 2062, 2128, and 2190, whilst the bands calculated by the formula $n=1/\lambda=(2113+66N)/\sqrt[6]{914/2 \times 270}=1937+60.5N$ are $\lambda\lambda$ 1937, 1997, 2058, 2118, and 2179.

J. F. S.

Two Peculiar Luminescence [Phenomena]. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1921, **21**, 45—65).—On illuminating certain preparations of zinc oxide with ultra-violet rays, a luminescence is displayed which slowly increases in intensity to a maximum, and on removing the exciting rays immediately disappears, but a dark, fading period must be present. A weak and transient phosphorescence is shown at the same time. Several liquids when mixed with this variety of zinc oxide display marked constitutive actions on the intensity of the luminescence. When potassium iodide is moistened with 2—5*N*-hydrochloric acid, it emits a luminescence which lasts for about one second and may be photographed. The wave-length of the luminescence waves lies in the region 300—313 $\mu\mu$. A similar effect may be produced by partly substituting for hydrochloric acid potassium chloride, bromide or iodide, or ethyl alcohol. The optimum mixtures have been determined in each case. Potassium iodide becomes at first more active by the absorption of water-vapour and then much weaker. The optimum effect is observed with a vapour pressure of water of 14.6 mm. at 25°. Inactive preparations are rendered feebly active by absorption of moisture. The phenomenon in all probability depends on a crystallo-luminescence brought about by the potassium chloride.

J. F. S.

Decomposition of Hydrogen Peroxide in Ultra-violet Light GERTRUD KORNFIELD (*Zeitsch. wiss. Photochem.*, 1921, **21**, 66—99).—Earlier measurements of the decomposition of hydrogen peroxide by ultra-violet light have shown that the Einstein equivalent law does

not hold for these cases, and further that the velocity of the process is dependent only on the quantity of light absorbed, and not on the concentration of the solution. The present work has as its object the investigation of the above-mentioned points. A series of measurements with non-homogeneous light of unknown wavelength was first made and found to be in keeping with the earlier work, since the velocity of the change is strongly reduced by small additions of acid or alkali. It was also found that a slight dependence of the reaction velocity on the concentration of the peroxide exists. The later experiments were made with light of wavelength 305–316 $\mu\mu$, and in each case the absorption was determined exactly. It is found that with increasing dilution the velocity is increasingly dependent on the concentration; the addition of acid also causes a diminution of the velocity which depends on the amount of acid added. That Einstein's equivalent law does not hold was confirmed, and it is shown that in the most favourable case $1 h\nu$ brings about the decomposition of eighty molecules. Assumptions are made as to the mechanism of the process, and these lead to calculated results which agree with the experimental results.

J. F. S.

Artificial Disintegration of Light Elements. (SIR) E. RUTHERFORD and J. CHADWICK (*Phil. Mag.*, 1921, [vi], 42, 809–825).—In previous papers (A., 1919, ii, 256–261; 1920, ii, 541) it was shown that when α -particles were passed through nitrogen, positively charged hydrogen atoms were liberated at high velocities, but an uncertainty remained as to the range of the hydrogen particle. With a new and improved microscope, the authors have now been able to show that the hydrogen particles emitted from nitrogen have a maximum range of 40 cm. of air, whereas the hydrogen particles from gaseous hydrogen or hydrogen compounds have a maximum range of 29 cm. of air, both being produced by α -particles from Radium-C of range 7 cm. of air. This proves definitely that the charged hydrogen particles do not come from either gaseous hydrogen or hydrogen compounds present as impurity in the nitrogen. The elements lithium, glucinum, boron, carbon, nitrogen, oxygen, fluorine, sodium, magnesium, aluminium, silicon, phosphorus, and sulphur or a suitable compound have been treated with α -rays from a quantity of Radium-C equivalent to 20 mg. of radium at a distance of 3.5 cm. from the zinc sulphide screen. The number of scintillations per minute per mg. activity of the source has been determined at an absorption of 32 cm. of air. It is found that boron, nitrogen, fluorine, sodium, aluminium, and phosphorus give off charged hydrogen atoms with ranges in cm. of air, of *ca.* 45, 40, *ca.* 40, *ca.* 42, 90, and *ca.* 65 cm. respectively. Chlorine, calcium, titanium, manganese, iron, copper, tin, silver, and gold give no particles of a greater range than 32 cm. of air, but no investigation has been made for particles of a range less than 32 cm. of air. In the case of nitrogen, it is shown that the number of particles emitted increases rapidly with the velocity of the α -particles. In the case of aluminium, it is found that the

direction of escape of the particles is to a large extent independent of the direction of the impinging α -particles, nearly as many being expelled in the backward as in the forward direction. The range of the backward particles is less than that of the forward particles; for example, with α -particles of range 7.0 cm. of air, the maximum range is 67 cm. of air for the backward particles but 90 cm. for the forward particles. It is shown that only those elements with an atomic mass of $4n+2$ or $4n+3$, where n is a whole number, give rise to hydrogen atoms. This result is explicable on the hypothesis that these elements are built up from helium and hydrogen nuclei. To account for the liberation of a hydrogen atom at high speed, it is necessary to suppose that the hydrogen nuclei are satellites of the main nucleus. In a close collision, the α -particle is able to give sufficient energy to the satellite to cause its escape at high speed from the central nucleus. The velocity of escape of the hydrogen atom does not seem to be very closely connected with the nuclear charge of the disintegrated element, for the range of the hydrogen atoms from boron (charge 5) is greater than that for nitrogen (charge 7), whilst the range of the hydrogen atom from aluminium (13) is greater than that from phosphorus (14). The above hypothesis assumes that positively charged substances attract one another at the very small distances involved. Such attractive forces must exist to hold the ordinary composite nucleus in equilibrium, and it seems likely that these attractive forces will extend some distance from the nucleus. If this view is correct, the forces on the α -particle are initially repulsive, but change sign very near the nucleus. Hydrogen atoms do not appear to be liberated from aluminium by α -particles of less range than 5 cm. This and the increased number liberated by an increase in the velocity of the α -particle shows that the "disruption" potential of the nucleus by an α -particle, that is, the potential difference required to communicate the same energy to an electron as is possessed by the α -particle, is of the order of six million volts for aluminium.

J. F. S.

Production of Radiation and Ionisation by Electron Bombardment in Pure and in Impure Helium. FRANK HORTON and ANN CATHERINE DAVIES (*Phil. Mag.*, 1921, [vi], **42**, 746-773).—An outline of the development of ideas concerning the arrangement of the two electrons in the helium atom is given, starting with the author's determination of the minimum radiation voltage and the minimum ionisation voltage for normal helium (A., 1919, ii, 210). In this connexion, the theoretical deductions of Bohr, Franck, and Reiche (A., 1920, ii, 656), Landé (A., 1919, ii, 309), and Kemble (this vol., ii, 478) are discussed and the experimental work of Compton (A., 1920, ii, 725) and of Franck and Knipping (A., 1920, ii, 72) is considered and criticised. Because of the divergence in the results of the various investigators, the authors' former conclusions have been re-investigated, in a specially designed apparatus, over a wider range of pressures than used before. The new experiments show that in pure helium radiation is produced

by the impacts of electrons with 20.4 volts energy, in confirmation of the authors' earlier conclusions, but in disagreement with the most recent conclusions of Franck and Knipping. A second type of radiation is produced at 21.2 volts, in agreement with Franck and Knipping. The 21.2 volt radiation ionises abnormal helium produced by 20.4 volts electron impacts, and with a relatively high gas pressure the detected effects of ionisation may swamp those of radiation. This result provides an explanation of the ionisation of helium by electrons having less than the normal ionising velocity, which is essentially different from that offered by Compton. Both types of radiation can be absorbed and subsequently re-emitted by normal helium atoms, so that they are passed from atom to atom throughout a volume of the gas. For velocities below the normal ionising velocity, the amount of ionisation produced as the result of electron impacts on abnormal helium atoms, under the experimental conditions, is small in comparison with that resulting from the ionising action of the 21.2 volts radiation. The possibility of the presence of a small quantity of impurity in the helium facilitating the production of radiation at 20.4 volts has been investigated, but no evidence that impurity acts in this way has been obtained. It is concluded that the significance of the experimental results in connexion with theories of the arrangement of the two electrons in the normal helium atom lies in the fact that they indicate that the limitations of the selection principle are not applicable to the fundamental displacements of the outer electron of the helium atom.

J. F. S.

J-Radiation. J. A. CROWTHER (*Phil. Mag.*, 1921, [vi], 42, 719-728).—The author has investigated the relative absorptibility of the primary and secondary X-radiations from an aluminium radiator. It is shown that the ratio of the secondary radiation to primary radiation steadily diminishes as the thickness of the absorbing screens is increased. This indicates that the secondary radiation is distinctly more absorbable than the primary. The coefficients of absorption of primary and secondary fluorescent radiations in aluminium have been determined for the radiators paraffin wax, aluminium, and copper. The author shows that the J-radiation, unlike the K-radiation, consists, not of a group of lines of approximately the same wave-length, but of a considerable number of lines comparatively widely spaced in the spectrum. The J-radiations from elements of low atomic number are very weak compared with the K-radiations. In the case of copper, the intensity of the hard, fluorescent radiation is about 1/30 of that of the characteristic radiation from the radiator. This indicates that these hard, fluorescent radiations are not easily excited. To excite any given line of the series it is probably necessary that the wave-length of the primary radiation should not be much shorter than that of the line to be excited. The hard secondary radiations produced from aluminium, copper, and paraffin wax probably correspond with different lines in the J-spectrum of the elements.

J. F. S.

Explanation of Röntgen Spectra and the Constitution of the Atom. L. VEGARD (*Physikal. Zeitsch.*, 1921, 22, 271—274), ADOLF SNEKAL (*ibid.*, 400—402).—Polemical. In the first paper Vegard replies to Smekal's criticism (A., 1920, ii, 654) of his theories on Röntgen spectra and the constitution of the atom (A., 1919, ii, 129). In the second paper Smekal maintains his earlier position.
J. F. S.

Wave-length of X-Rays. RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1921, 11, 366—373).—A theoretical paper in which it is shown that with the existing knowledge it is impossible to determine definitely the structure of any crystal in advance of a knowledge of the wave-length of X-rays. Viewed from this position alone, the problem of the length of X-ray waves and of the structures of crystals becomes indeterminate. If the case of sodium chloride be taken as typical, it is shown that there are other structures, beside the commonly-accepted "sodium chloride arrangement," which are in agreement with the present experimental data. As a result of this lack of definiteness, it is emphasised that it is more logical to consider the value of the wave-lengths of X-rays as based on the quantum hypothesis.
J. F. S.

The Mass Absorption and Mass Scattering Coefficients for Homogeneous X-Rays of Wave-length between 0.13 and 1.05 Angström Units in Water, Lithium, Carbon, Nitrogen, Oxygen, Aluminium, and Iron. C. W. HEWLETT (*Physical Rev.*, 1921, 17, 284—301).—The presentation of new experimental work is preceded by a discussion of the current views of the mechanism of absorption and scattering. The total absorption coefficient of homogeneous X-rays, obtained by means of a Bragg spectrometer, was measured for the above-named materials at various wave-lengths. The total mass absorption coefficient was found to be proportional to the cube of the wave-length over certain regions, but in all cases where the above range was entirely covered, the constant of proportionality differed for different ranges of wave-length. The case of hydrogen seems to be an exception, as its total mass coefficient was found proportional to the $9/2$ power of the wave-length. This, however, was obtained by combining the results from water and liquid oxygen. The constant with which the cube of the wave-length is multiplied to give the true mass absorption coefficient is found to be approximately proportional to the cube of the atomic number of the absorbing element, except for lithium, indicating that Moseley's law does not hold for that element. The true mass absorption coefficient for iron is apparently not proportional to the cube of the wave-length between 0.70 and 1.05 Å.U. For other elements with wave-lengths less than 0.20 Å.U., these coefficients are smaller than is to be expected from theory if the electron has a diameter of the order of 10^{-12} cm. The lack of this decrease in the coefficients of iron is attributed to a shrinkage in the diameter of the electrons in the atoms on account of a closer packing of the electrons. The mass scattering coefficient

of all the materials studied is less than that given by Thomson's theory. For hydrogen it is approximately twice that for other elements, which is further evidence that hydrogen has twice as many scattering electrons per unit of mass as other elements. For iron this coefficient apparently increases for wave-lengths longer than 0.70 Å.U.

CHEMICAL ABSTRACTS.

A Radioactive Quantity requiring a Name. N. ERNEST DORSEY (*J. Washington Acad. Sci.*, 1921, 11, 381-386).—The author puts forward reasons for introducing a new radioactive quantity. The main reason is to avoid the use of long sentences in expressing the quantity of a radioactive substance used, such as "Radium-C corresponding with 1 gram radium." The quantity which the author terms "*r*" is that amount of the material which will produce transformed atoms at the same rate as transformed atoms are produced by 1 gram of radium. The author proposes that either the present definition of the curie be modified to meet the case, or a new unit, termed the *rutherford*, be introduced.

J. F. S.

Application of Anode Rays to the Investigation of Isotopes. G. P. THOMSON (*Phil. Mag.*, 1921, [vi], 42, 857-867; cf. *Proc. Camb. Phil. Soc.*, xx, 210).—Photographs have been obtained for anode rays showing parabolas corresponding with singly charged atoms of lithium, glucinum, sodium, potassium, calcium, and strontium. Lithium is a mixture of isotopes of atomic weights 6 and 7. The proportions in which these appear in the rays are not constant, there being a tendency for the line at 6 to be sometimes considerably stronger than would be expected from the atomic weight. Glucinum is apparently single, atomic weight 9. If there is an isotope at 10 or 11, it is present in extremely small proportion. The remaining elements could not be resolved with the apparatus used, but calcium must consist of atoms of weight equal to those of either potassium or argon, that is, a so-called "isobar." No trace was found of doubly-charged metallic atoms or of atoms with a negative charge. It seems probable that the mechanism of the anode rays is more analogous to spluttering than to electrolysis.

J. F. S.

Branching Relationship for Ra-C, Ac-C, Th-C, and the Disintegration Constant of the C' Products. ELEANORE ALBRECHT (*Chem. Zentr.*, 1921, iii, 516; from *Sitzungsber. K. Akad. Wiss. Wien*, 1919, [2A], 128, 925-944).—Making use of Marsden and Darwin's (A., 1912, ii, 824) relationship $\text{Th-C}' : \text{Th-C} = 0.35$, the author has determined the corresponding branch relationship for Ac-C and Ra-C. The C' products were obtained by the recoil method from very active C products. From the electrometric measurements, the half life (*T*) has been calculated and the following values have been obtained, Ac-C', *T*=4.76 min., Th-C', *T*=3.20 min., and Ra-C', *T*=1.32 min. The C' products were collected on a negatively charged brass disk, which was placed above and very close to another plate containing the C products. A residual

activity, which is due to a contamination of the C'' plates by $Ac(B+C)$, $Th(B+C)$, or $Ra-C$ respectively, is estimated and brought into the calculations, so that a pure disintegration curve of the C'' product is obtained. The branching relationship, $Ac-C'' : Ac-C$ is calculated from the ionising relationship of $C'' : C$, on the assumption that in the appropriate equations one pair of proportionality factors varies as the ionising action of the α -particles of $Ac-C$ and $Th-C$, whilst the second pair varies as the absorption coefficients of the β rays of $Ac-C''$ and $Th-C''$. The relationships found are $Ac-C'' : Ac-C = 99.84$ and $Ra-C'' : Ra-C = 0.0004$.

J. F. S.

Nomenclature of the Radioactive Families. M. C. NEUBURGER (*Physikal. Zeitsch.*, 1921, 22, 247—248).—The author proposes a modified nomenclature for the radioactive families; this includes the terms, principal family, root family, and branch family. The principal families are the uranium and thorium families, and include the whole of the products of disintegration of these elements respectively. The root family, and there is only one, is that portion of the uranium family before the branching into ionium and uranium- Y ; it consists therefore of the series $U_1 \rightarrow U-X_1 \rightarrow U-X_2 \rightarrow U_2$. There are two branch families, namely, ionium \rightarrow the final products, and uranium- $Y \rightarrow$ the final products.

J. F. S.

States of Iron in Nitric Acid. JOSEPH GRANT BROWN (*J. Physical Chem.*, 1921, 25, 429—454).—The author has measured the *E.M.F.* of cells of the type $Fe|HNO_3 \text{ soln.}||HNO_3(\text{conc.})|Pt$, in which, the nitric acid varied between d 1.01 and 1.41 and the iron electrode was sometimes rotated and sometimes still during the measurement. The *E.M.F.* was measured repeatedly from the moment of immersion of the electrode until a steady state was obtained. The surface of the electrode in the motionless experiments was examined microscopically. The results are discussed at length and the author is of the opinion that active iron is ferrous, that is, it sends ferrous ions into the solution, whilst passive iron is ferric.

J. F. S.

The Theory of the Pile. DÉCOMBE (*Compt. rend.*, 1921, 473, 834—836).—The author proposes to base the theory of the hydroelectric pile on the proposition that the non-compensated heat developed in a pile in action by the chemical reaction proceeding in it is equal to the Joule heat, ri^2dt , which is developed therein by virtue of its internal resistance r and of the current i which is circulating. This is discussed from a theoretical point of view.

W. G.

Potential of the Thallium Electrode and the Free Energy of Formation of Thallous Iodide. GRINNELL JONES and WALTER CECIL SCHUMB (*Proc. Amer. Acad. Arts Sci.*, 1921, 56, 199—236).—Measurements have been made at 25° and 0° of the conductivity and ionisation of thallous nitrate solutions, of the solubility of thallous chloride and of thallous iodide, and of the normal potential

of the thallium and the iodine electrodes. From the conductivity data the equivalent conductance of the thallium ion was found to be 78.36 mhos at 25° and 41.8 mhos at 0°. The equivalent concentrations of the ionised fractions of thallous chloride and thallous iodide, calculated from the conductivity of saturated solutions of these salts, are, respectively, 0.014094 and 0.000235 at 25°, and 0.006095 and 0.0000587 at 0°. From the potential measurements it has been computed that the normal potential of the thallium electrode is +0.6188 volt at 25° and +0.5885 volt at 0°, and that of the iodine electrode -0.3406 volt at 25° and -0.3399 volt at 0°. From the foregoing results, the following are computed for the reaction: $\text{Tl (solid)} + 0.5 \text{I}_2 \text{ (solid)} = \text{TlI (solid)}$: free energy of formation (Δ) = 125.79 kj. at 25° and 125.48 kj. at 0°; heat of formation (U) = 122.11 kj. at 25°. Contrary to the assumptions of earlier investigators, it has been found that a metallic thallium electrode is more negative than a saturated two-phase amalgam electrode by 2.8 millivolts at 25° and 1.8 millivolts at 0°.

CHEMICAL ABSTRACTS.

Electrolysis of Hot Concentrated Sulphuric Acid. HANS HOFFMANN (*Zeitsch. Elektrochem.*, 1921, 27, 442-445).—The author has electrolysed concentrated sulphuric acid (98.3%) d_4^{20} 1.841 at a series of high temperatures by currents of various strengths. It is shown that at 50°, independently of the current strength, hydrogen, hydrogen sulphide, and sulphur are produced on the cathode, whilst at higher temperatures sulphur dioxide and sulphur are produced and in the neighbourhood of 300° only sulphur is obtained. Oxygen is liberated from the anode at these temperatures. At 200°, the oxygen is mixed with sulphur dioxide, produced from sulphur which has diffused from the cathode chamber, and has been oxidised by the hot sulphuric acid and the nascent oxygen. From 280° upward sulphur dioxide and oxygen are liberated in quantities corresponding with Faraday's law. The gas element SO_2/O_2 , in consequence of incomplete charging of the electrodes, does not furnish the expected *E.M.F.*, and also the velocity of reaction of the gases is too small for the production of large quantities of current. The technical possibilities of such a cell are regarded as hopeless. The decomposition voltage of hot concentrated sulphuric acid lies near to that of water, that is, higher than the calculated and observed values of the potential difference of the gas element. From this it follows that the primary products of electrolysis are hydrogen and oxygen whilst sulphur dioxide is a secondary product.

J. F. S.

Structure of Metal Electrolytically deposited on Rotating Cathodes. W. E. HUGHES (*J. Physical Chem.*, 1921, 25, 495-509).—A discussion on the structure of metals which have been deposited electrolytically on rotating cathodes. It is suggested (1) that the polished appearance often observed on the surface of deposits formed on rotating cathodes is due to the smallness of the grains

composing the deposit, (2) that the smallness of grain is a consequence of the constancy of metal concentration at the cathode surface, and (3) that, since mechanical movement can maintain a constant metal concentration, rotation of the cathode operates in that way in the cases of deposits formed on rotating cathodes and not, as has been suggested, by way of burnishing. J. F. S.

Influence of Chlorides on the Decomposition Voltage Curve of Chromic Acid. E. LIEBREICH (*Zeitsch. Elektrochem.*, 1921, 27, 452—455).—The thin layers of oxide or hydroxide on the cathode which give rise to the periodic phenomena observed during the electrolysis of chromic acid are shown to be colloidal in nature; the oxide is drawn to the cathode just so long as a negative tension lies on it. The addition of chlorides brings about a displacement of two curves which make up the decomposition voltage curve of chromic acid. J. F. S.

Calculation of the Specific Heat of Gases. II. W. HERR (*Zeitsch. Elektrochem.*, 1921, 27, 474—475; cf. this vol., ii, 299).—A theoretical paper in which the author has deduced four equations by means of which the difference between the two specific heats of gases may be calculated. The first of these, $C_p - C_v = \gamma/M^{1/3}d^{1/3}$ ($T_k - T$) in which γ is the surface tension is deduced from the Eötvös rule for non-associated liquids. According to Lorenz (A., 1916, ii, 240), the quotient of the density at the boiling point and the critical density is approximately equal to 2.66, whence the second equation, $C_p - C_v = 0.75d_s/d_k M$, is obtained. The third equation, $C_p - C_v = cL/MT_k^2$, in which c is the boiling-point elevation constant and L the latent heat of vaporisation, is obtained from van't Hoff's boiling-point relationship. The fourth equation is obtained by combining Eötvös's rule with Oswald and Davies's equation, $T_k = (1/K_{20} + 293)/2$ (*Zeitsch. anorg. Chem.*, 1920, 112, 278). This has the form $C_p - C_v = (1/K_{20} + 273)/MT_k$, in which K_{20} is the coefficient of expansion at 20°. The values of $C_p - C_v$ calculated by each of these equations is compared with the experimentally determined values of twelve substances of widely differing character; a fair agreement is found in all cases. In the first equation, the variations from the accepted value lie between +5.5% and -12%, in the second equation between +6% and -27%, in the third equation between +6% and -21%, and in the fourth equation between +2% and -18%. J. F. S.

Fielding's Formula connecting Critical Temperatures and Pressures. J. NEWTON FRIEND (*Chem. News*, 1921, 123, 219—220).—The author shows that the formula recently put forward by Fielding (A., 1919, ii, 45) connecting critical temperature with critical pressure has a theoretical basis and may be evolved from the van der Waals equation. The formula has the form $T_c = K\sqrt{p_c} + x$, in which K and x are constants. The author shows that the expression $T_c = 8/R\sqrt{xp_c}/27$ is readily obtained. If now \sqrt{x}/K remains fairly constant, as is quite possible at least for allied elements, the equation may be written $T_c = K\sqrt{p_c}$, where K is a

constant equal to $8\sqrt{\alpha}/R\sqrt{27}$. This expression is the essential feature of Fielding's equation, and since it is not to be expected that $\sqrt{\alpha}/R$ is even approximately constant for all the elements, it is not surprising that Fielding finds notable exceptions to his formula. Hence there is not only a theoretical basis for the formula but also an explanation for the exceptions. J. F. S.

Latent Heat of Vaporisation. J. C. THOMPSON (*Chem. News*, 1921, 123, 204—206).—On the bases of several unusual assumptions, the author deduces a formula for calculating the latent heat of vaporisation. The formula has the form $P \log_{10} P / 10.31 \times D^{1.3} = L$, in which P is the ratio between the density of a liquid and its vapour at the boiling point, and D is the density of the liquid at the boiling point compared with water at 4°. The assumptions made in the deduction of the formula are: (i) molecules do not collide, but pass sufficiently near to each other for the forces of attraction between them to be constantly altering the direction of movement. The forces of attraction probably consist of ordinary gravitational force together with surplus or unsaturated valency force, (ii) molecules are without size, (iii) a liquid is merely a gas under the pressure produced by the attractive force of its molecules, (iv) a solid is a liquid in which the attractive forces of the molecules are different in different directions, (v) a crystalline solid is a solid in which the major attractive forces are all acting in one direction, and the minor forces in another. The values calculated for the latent heat by means of the above formula agree remarkably well with the accepted experimental values; thus: water 536.6 (536.6), ethyl ether, 87.58 (87.4), benzene, 95.21 (96.1), and oxygen, 52.3 (52.0); the accepted values are given in brackets. J. F. S.

Specific Heat of Vapours. Determination of Specific Heat of a Vapour at Constant Pressure, Cp. J. C. THOMPSON (*Chem. News*, 1921, 123, 220—221).—A theoretical paper in which a method of calculating the specific heat of gases at constant pressure is outlined, which, although not theoretically sound, yields fairly correct results. The axioms (i), (iii), (iv) in the preceding abstract and those following are discussed. (a) The size of molecules does not in any way influence the volume occupied by a liquid. (b) A crystalline solid is so arranged that equal forces always act in the same direction. The growth of a crystal from solution is explained on this hypothesis, as the molecules in separating from solution will attach themselves to the small crystal so that the greater forces act on the greater forces. J. F. S.

Necessity of bringing Concordance into the Thermochemical Data of Organic Compounds. WOJCIECH ŚWIĘTOSŁAWSKI (reprint from *Roczniki Chemji*, 1, 59—103).—The author reviews a large number of thermochemical data of organic compounds and discusses the experimental basis of the results. He maintains that a single organic substance ought to be chosen as the standard of thermochemical data; this substance should be benzoic acid, the heat of combustion of which should be determined

with the greatest precision and the value obtained accepted as an international standard. The value ought to be expressed in calories and not in absolute units, since it is impossible to determine the latter quantity with the necessary precision. Calorimetric bombs should always be standardised by means of this substance, and authors of work in the thermochemistry of organic compounds should always state full details of the standardisation of the bomb so that recalculation of the results may be possible.

J. F. S.

Divergence between Adiabatic and Ordinary [Thermochemical] Measurements. W. SWIENTOSŁAWSKI and HELENA I ZOFJA BŁASZKOWSKIE (*Roczniki Chemji*, **1**, 166—170).—The authors have carried out thermochemical measurements under differing conditions; (1) in an ordinary calorimeter in which the temperature of the outer jacket was kept constant; (2) in an ordinary calorimeter in which the evaporation of water was prevented by covering it with a layer of a very slightly volatile liquid; and (3) in an adiabatic calorimeter. The results obtained show that the figure obtained by the measurement of a constant quantity of heat in an ordinary calorimeter differs from the value obtained for the same quantity in an adiabatic calorimeter according to the conditions under which the measurement is made. The difference in the two values varies between $\pm 0.03\%$ and $\pm 0.46\%$.

J. F. S.

Substantive Cotton Dyeing. RUDOLF AUERBACH (*Kolloid Zeitsch.*, 1921, **29**, 190—193).—The velocity of diffusion of a number of substantive cotton dyes into a 4% gelatin jelly has been determined at 20°. The distance to which the dye has diffused was measured after twenty-four, thirty-six, sixty, and eighty-four hours and comparative measurements were made with 0.1, 0.05, and 0.01% solutions of the highly-dispersed crystal-violet. It is shown that dyes which are adsorbed from cold solution, diffuse at an average rate of 3.5 mm. per day from 0.1% solutions, whereas dyes which are adsorbed from warm solutions under the same conditions diffuse at 0.9 mm. per day. Potassium dichromate will also dye cotton, but if the dyed material is washed with either water or alcohol the dichromate is all removed, but in washing with mixtures of alcohol and water it is found that less dichromate is removed as the alcohol concentration increases up to a maximum alcohol concentration of about 65%, after which more dichromate may be washed out. It is suggested that the dispersion of the dichromate is at its minimum in the presence of 65% alcohol.

J. F. S.

The Empirical Formula of Walden and the Theory of Ghosh. (MLLE) H. KADICOVÁ (*Chem. Listy*, 1921, **15**, 109—110).—The values obtained for the empirical constant of Walden (A., 1920, ii, 598—600) $D\sqrt{v}$ as determined by himself and those resulting from calculations according to Ghosh's theory (T., 1918, **113**, 449; 1920, **117**, 1390) for different degrees of dissociation, although in close agreement, are not identical. Since

a comparison of the results of both Walden and Ghosh leads to the conclusion that for a definite degree of dissociation the value of $D\sqrt{v}$ is a constant, it may also be concluded that an electrostatic attraction really exists in solution between electrolytic ions having charges in agreement with the charge of ordinary electrons. The supposition of Ghosh that strong electrolytes are completely dissociated especially in concentrated solutions does not seem warranted.

CHEMICAL ABSTRACTS.

Bragg's Work and the Law of Definite Proportions. A. QUARTAROLI (*Gazzetta*, 1921, 51, ii, 211—212).—The author replies to Perucca's criticism (this vol., ii, 493) on his previous paper (A., 1920, ii, 602). T. H. P.

Possible Utilisation of the Diagrams of Diffraction of X-Rays for the Complete Determination of the Structure of Quartz. CH. MAUGUIN (*Compt. rend.*, 1921, 173, 719—721).—A discussion of the results obtained by radiograms prepared according to Laue's method with a consideration of their use in calculating the value of the parameters used by Bragg in his definition of the structure of quartz. W. G.

X-Ray and Infra-red Investigations of the Molecular Structure of Liquid Crystals. J. STEPH. VAN DER LINGEN (*J. Franklin Inst.*, 1921, 192, 511—514).—A thin pencil of X-rays has been passed through a thin layer of *p*-azoxyanisole and the pattern produced examined. In the case of the solid substance irregularly placed spots are observed which indicate that the crystalline layer is made up of small crystal units of about 1 mm. cross-section. On heating until the *p*-azoxyanisole is plastic and again examining the pattern, it is found that a point pattern is obtained which gives no indication of the type of the crystal symmetry. On heating further until the anisotropic liquid is obtained, a new type of pattern is observed consisting of a series of faint horizontal lines, which are about 1 mm. broad for those lines which pass through the central spot; further off they are fainter, thinner, and more closely spaced. If this is due to diffraction from parallel layers of lamellar molecules, the spacing between the molecules must be of the order 40 Å.U. The absorption spectra of solid, anisotropic liquid, and amorphous liquid forms of *p*-azoxyanisole and the ethyl ester of *p*-azoxycinnamic acid have been examined for infra-red light. It is shown that in all cases the spectra are alike, hence no change has taken place in the linking of the atoms in the molecule. If changes in the space lattices be due to changes in the molecules of polymorphous substances, then these changes are not due to changes in the radicles, but to a spatial rearrangement of the component parts of the molecules. J. F. S.

The Hydroxyl Ring. H. T. F. RHODES (*Chem. News*, 1921, 123, 249—250).—A continuation of the author's previous work on the constitution of crystal hydrates (this vol., ii, 255). In the present paper, the constitution of the molecule of crystalline copper

sulphate is considered. The author considers that one molecule of water differs from the remaining four, because on treating the pentahydrate with ammonia, only four molecules of water are replaced by ammonia to form the tetra-amminomono-hydrate of copper sulphate, whilst treating the penta-ammino derivative with water all five ammino-groups are replaced by water. It is shown that, with the exception of a few special cases, the hydrates of salts may be classed in four types of different constitution. J. F. S.

Is there Redissolution of Sodium Chloride in the Presence of a Non-congruent Solution submitted to Evaporation? C. RAYEAU (*Compt. rend.*, 1921, 173, 772; cf. this vol., ii, 31, 386).—A further reply to Rengade (cf. this vol., ii, 93). W. G.

Ionic Synergism. I. Experiments with Congo-rubin. L. MICHAELIS and C. TIMÉNEZ-DIAZ (*Kolloid Zeitsch.*, 1921, 29, 184—190).—It is shown that in all the work on the influence of ions on the condition of colloids the influence of the ions of the solvent has been disregarded. Experiments have been carried out on solutions of congo-rubin to ascertain the influence of a number of sodium and potassium salts in the presence of known concentrations of hydrogen ions. It is shown that each individual type of kation has an action of characteristic strength on the condition of a colloid, which may be experimentally determined for the hydrogen ion, but can only be determined for the sodium or potassium ion by extrapolation for an infinitely small hydrogen-ion concentration of the solvent. The hydrogen and sodium or potassium ions in mixtures do not influence the activity according to an additive law, but rather according to the law that all combinations of these ions have the same action for which $(\log h_0/h) \cdot (\log i_0/i) = \text{constant}$. In the equation h is the concentration of hydrogen ions and i that of the alkali ions. The significance of h_0 and i_0 is seen as follows: if the condition of the reversible colloid solution is represented by Z , then, for a mixture of hydrogen ions of concentration h and alkali ions of concentration i , $Z=f(h.i)$. If to change the condition to z in a definite time, a mixture of hydrogen ions, h_z , and alkali ions, i_z , is necessary. Then $h_0 = \lim h_z$ when $i=0$, and $i_0 = \lim i_z$ when $h=0$. h_0 and i_0 are the asymptotes of the hyperbola represented by the equation $(\log h_0/h) \cdot (\log i_0/i) = k$, and have the values $h_0 = 10^{-1/2}$ and $i_0 = 10^{-1/2}$. The sodium and potassium ions behave in mixtures as though they were of the same type. The combination of calcium and hydrogen ions appears to follow a similar law to that obtaining for the alkali ions. J. F. S.

Dielectric Constants of Colloidal Solutions. RUDOLF KELLER (*Kolloid Zeitsch.*, 1921, 29, 193—196).—The dielectric constant of a number of colloidal solutions has been determined by Drude's method. It is shown that solutions of hydrated colloids such as gelatin and albumin in certain circumstances exhibit abnormally low dielectric constants, whilst colloidal gold solutions have still lower values. The colloidal solutions which occur in natural organisms and contain electrolytes show occasionally an exceed-

ingly high dielectric constant. The terms acidic and basic lose their classical meaning in non-dissociated and associated solutions, since only dissociated solutions can be acid or basic. Not only dyes, albumin, and amphoteric substances, but also potassium hydroxide and hydrochloric acid in the region of medium dielectric constant are somewhat associated, that is, colloidal; at most they are molecular dispersed and not ion dispersed. They obtain the sign of their charge, not from their internal chemical constitutive properties, but from their relative surface charge toward the dispersion medium. Potassium hydroxide in positively charged toluidine is to be regarded as electro-negative, whilst hydrochloric acid in benzaldehyde is positive.

J. F. S.

Colloidal Condition of Sparingly Soluble and Slightly Soluble Substances in Water and other Solvents: Experimental Confirmation of Gibbs's Principle. I. TRAUBE and P. KLEIN (*Kolloid Zeitsch.*, 1921, 29, 236–246).—An examination of solutions of sparingly soluble substances such as aqueous solutions of hydrocarbons, alkyl haloids, higher alcohols and aliphatic acids, *i*-amyl alcohol, *i*-butyric acid, aniline, *m*-cresol, lead and calcium sulphates, silver chloride, and silver oxalate, by means of the Tyndall cone and the ultra-microscope, shows that the whole of such substances are partly or entirely colloidally dissolved. It appears to be general that in the solution of easily-soluble substances such as sodium chloride in water the transition from the solid homogeneous phase to the solution takes place in such a way that submicrons exist for a short period in the saturated solution. The above is probably true for solvents other than water; thus a solution of water in benzene or carbon tetrachloride shows a colloidal phase. The very poor surface activity of hydrocarbons and alkyl haloids in stalagmetric investigations is to be attributed to the coarse dispersion. The diameter of a larger submicron is of the order 10^{-5} cm., whilst that of an individual molecule is 10^{-8} cm., so that the surfaces stand in the ratio $10^{-10}:10^{-16}$. Such substances in solutions as submicrons only show greater surface activity, despite the strong Gibbs's positivity, when they are converted into molecules or the densest emulsions. The first case is observed with bases such as atropine and acids such as nonoic acid, and the second with indifferent narcotics such as chloroform. If the Traube narcosis hypothesis is substituted for Gibbs's positivity, then all abnormalities can be explained. It is shown by means of the ultramicroscope that surface active substances accumulate, in accordance with Gibbs's principle, at the interface, oil-water, air-water, and lecithin-water. The fall of concentration increases with the size of the Gibbs's positivity. Gibbs's negative substances do not show this accumulation, for in some cases the concentration decreases in the region of the surface. Sparingly soluble benzene derivatives such as xylydine and cresol are very highly colloidal, a fact which explains the ease with which such substances are adsorbed by charcoal. Investigation of the cataphoresis of such substances shows that the colloidal

particles of aniline, toluidine, xyloidine, octoic acid, and nonoic acid migrate to the anode, whilst quinoline migrates to the cathode. Preliminary experiments in the adsorption of poisons by the surface of cells of blood corpuscles, yeast-cells, and bacteria-cells have been made, from which conclusions on the cell-destroying action of these substances may be drawn.

J. F. S.

Precipitation of Colloids by Non-electrolytes. PAUL KLEIN (*Kolloid Zeitsch.*, 1921, 29, 247—250).—The results of experiments on the coagulation of colloids by non-electrolytes are described. It is shown that, in the absence of electrolytes, surface active non-conductors are able to coagulate negatively-charged colloids (suspensions and emulsoids). In some unpublished work, Traube has shown that suspensions of charcoal and sulphur are coagulated by surface active non-electrolytes as soon as the water is saturated with these substances. The same action is now observed for sols of negatively-charged colloids such as arsenic sulphide, albumin, gold, silicic acid, and mercury sulphide. In these cases, coagulation only takes place when the surface active substance in the finest possible state of division in alcohol solution is added to the colloid. Electro-positively charged sols such as ferric hydroxide and aluminium hydroxide are not coagulated under the above-named conditions. The coagulation of albumin by narcotics is irreversible as long as any of the narcotic remains adsorbed in the albumin. This fact will probably furnish the reason for the harmful and sometimes fatal action of narcotics. Coagulation by sparingly soluble surface active non-conductors probably takes place in two phases. The first phase consists in a reduction of the degree of dispersion by mutual coagulation of two colloids, whilst the second consists in the adsorption of the larger particles on the surface of the separated drops of the non-conductor. This view demands that the primarily-formed colloid of the non-conductor should have a positive charge.

J. F. S.

Quantitative Methods of Coagulation for Suspensions. FRIEDRICH VINCENTZ VON HAHN (*Kolloid Zeitsch.*, 1921, 29, 226—236).—Since the stability of suspensions is determined almost entirely by means of the coagulation by electrolytes, by one or other of the methods, (a) the drop process (Schulze), (b) the titration process (Linder and Picton), (c) the mixture process, and since different investigators using these methods obtain widely differing results, the author has investigated these and other methods in the case of arsenic sulphide sols. It is shown that the mixture process is the most convenient, but the Schulze precipitation method has the advantage that very little (5 c.c.) of the sol is required for a determination. The titration process is not suitable for quantitative work, because the rate of addition of the electrolyte has a marked influence on the result. The author recommends the use of potassium chloride as a normal electrolyte for such determinations. Since it is quite possible that the electrolyte coagulation method is not suitable in all cases, for example, in the case of very dilute

sols or in those cases where chemical combination occurs between the sol and the coagulating electrolyte, the author has tested other methods of coagulation, which include, (1) the effect of filtration on the sol, (2) effect of boiling, and (3) the effect of an electric current. Filtration influences a sol in the sense of causing an increase of the size of the particles. Particularly in the case of very dilute sols it is possible to obtain trustworthy data on the stability of the sol by making a partition curve of the sediment obtained from a series of successive filtrations. An approximate measure of the stability of a sol can be obtained by placing a drop of the sol on a filter-paper and measuring the ratio of the radius of the surface moistened by the unchanged sol to that of the surface moistened by the dispersion medium. This ratio, termed the "capillary number," is characteristic of the sol. The boiling test of stability is very easily carried out, but the method is not suitable for dilute sols, and is only to be regarded as a confirmatory test to the electrolyte coagulation method, or as a substitute for this in cases where chemical reaction occurs between the electrolyte and the sol. Experiments make it likely that coagulation by boiling depends on an adsorption process at the liquid vapour interface. The time required by a definite current to effect coagulation of a sol can be used as a measure of the stability.

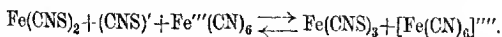
J. F. S.

Emulsions. III. Further Investigations on the Reversal of Type by Electrolytes. SHANTI SWARUPA BHATNAGAR (T., 1921, 119, 1760—1769).

Graphical Representation of certain Heterogeneous Equilibria. A. C. D. RIVETT (*Chem. News*, 1921, 123, 251—252).—A theoretical paper in which it is shown that the usual method of graphical representation of equilibria in binary and ternary heterogeneous systems often expresses relationships which are in opposition to the principles of the phase rule. A modified method of representation which avoids such anomalies is put forward.

J. F. S.

The Oxidation of Ferrous Salts by Potassium Ferricyanide. M. HANNIK (*Chem. Weekblad*, 1921, 18, 615—616).—The experiments were made with solutions containing 0.007163 gram-molecule of reagent per litre, in presence of concentrated ammonium thiocyanate solutions; the equilibrium examined was therefore



The ferric thiocyanate formed or remaining in the solution (the equilibrium position was determined from both end-systems) was determined colorimetrically.

The oxidation of the ferrous salt was found to be almost quantitative, completely so in presence of excess of either reagent (ferrous salt or ferricyanide). The reverse reaction proceeds to a small extent only even in the presence of excess of ferrocyanide. In the

ordinary preparation of Turnbull's blue, the equilibrium is affected by the action of the ferrocyanide formed on the ferrous salt present.
S. I. L.

Landolt's Reaction. II. Some Reactions Analogous to the Landolt Reaction. J. EGGERT and B. SCHARNOW (*Zeitsch. Elektrochem.*, 1921, 27, 455—470).—It was previously found in the kinetic investigation of the Landolt reaction, which takes place according to the equations, (1) $\text{IO}_3' + 3\text{SO}_3'' = \text{I}' + 3\text{SO}_4''$, (2) $\text{IO}_3' + 5\text{I}' + 6\text{H}' = 3\text{H}_2\text{O} + 3\text{I}_2$, (3) $\text{I}_2 + \text{SO}_3'' + \text{H}_2\text{O} = \text{SO}_4'' + 2\text{I}' + 2\text{H}'$, that the iodine-ion formation up to the liberation of free iodine takes place according to the equation $t = 1/(k_2 - k_1) \log_e (1 + (k_2 - k_1)x/k_1a)$, where k_1 and k_2 are the reaction constants of (1) and (2) respectively. The equation $T = 1/(k_2 - k_1) \cdot \log_e k_2/k_1$ holds for the turning point where all the sulphite-ion has been used up, that is, where $x = a$. The time of the turning point is therefore independent of the concentration of the sulphite-ion, but inversely proportional to the concentration of the iodate-ion. The object of the present investigation is to find whether, by employing other reducing agents than sulphurous acid, the more general case exists, namely, that in which the third partial reaction is also determinative of the time of the turning point. For this purpose, the reducing agents potassium ferrocyanide, arsenious acid, sodium thiosulphate, and hydroxylamine hydrochloride have been examined. It is shown that, with respect of the Landolt reaction, reducing agents may be divided into two groups; to the first of these, thiosulphate and sulphite belong. In these cases, the third reaction takes place more rapidly than the second all through the process, that is, at the turning point the reducing agent is all used up. Ferrocyanide and arsenite constitute the second group, and in these cases the third reaction may proceed more slowly than the second, that is, at the turning point only a portion of the reducing agent has been used. Hydroxylamine is a particular case in which the second reaction proceeds more rapidly than the first, and in consequence the Landolt effect is not observed. In the case of the reducing agents in the second group, the equation $t = 1/(k_2 - k_1) \cdot \log_e \{1 + (k_2 - k_1)x/k_1a\}$ again holds, with the difference that at the turning point x is no longer equal to a but $x = na$, where n is a fraction representing the ratio between the amount of reducing agent used to the original quantity added. The experiments with these reducing agents show that the time of the turning point is independent of the initial concentration of the reducing agent, but inversely proportional to the iodate-ion concentration. Despite the fact that the whole of the reducing agent has not been used at the turning point, the Landolt effect is exhibited. The theory of the reaction demands, (1) that n shall be constant, (2) that the constants k_1 and k_2 shall be proportional to the iodate-ion concentration, and (3) that the velocities at the turning point are proportional, (a) for constant iodate-ion concentration, to the ferrocyanide-ion concentration, and (b) for constant ferrocyanide-ion concentration, to the iodate-ion concentration. These demands are fulfilled in

the case of ferrocyanide-ion and arsenite-ion. Whilst the constants k_1 and k_2 are of the same order in the ferrocyanide reaction, the mean relationship k_2/k_1 is 8.4×10^{-3} in the arsenite reaction, that is, the second reaction is 8000 times as rapid as the first. In the reaction between the iodate-ion and the thiosulphate-ion, the main reaction products are the sulphate-ion and the tetrathionate-ion, which demands a new method of calculating k_1 and k_2 and furnishes a new confirmation of the theory. Along with the ions named, an undetermined oxidation product of the thiosulphate is produced which reacts slowly with iodine to form sulphate. In consequence of the small amount (1.2%) of this product, the mechanism of the reaction is only slightly influenced. In the reaction between the iodate-ion and the hydroxylamine-ion, iodine is separated on mixing the reagents, but the blue coloration of the starch only takes place when the velocity of reaction $2\text{NH}_2\text{OH}' + 2\text{I}_2 = \text{N}_2\text{O} + \text{H}_2\text{O} + 6\text{H}' + 4\text{I}'$ has become great enough to raise the iodine concentration to 10^{-6} gram per litre, that is, to the smallest amount recognisable by starch solution. The delayed blue coloration does eventually appear even in this case, but for quite other reasons, so that this reaction cannot be included in either of the other groups.

J. F. S.

Intra-molecular Energy during Combustion. W. T. DAVID (*Phil. Mag.*, 1921, [vi], 42, 868—870; cf. A., 1920, ii, 82, 731; this vol., ii, 85).—A continuation of previously published work. In the present paper, the pre-pressure period and the explosion period of coal gas explosions are considered. The pre-pressure period is the interval between the time at which the igniting spark passes and that when the pressure commences to rise. In this interval, a considerable amount of gentle ignition occurs, but there is no rise of pressure. In the cases considered, the number of molecules after explosion is about 3% less than before combustion, consequently the translational energy of the freshly-formed molecules during this period is not greater than that of the molecules before ignition. There is no appreciable radiation emitted in this period. In the early stage of the explosion period, the pressure rises slowly, indicating that combustion is proceeding slowly and a small but appreciable radiation is emitted. The radiation of longer wave-length up to about 11μ is emitted first, and then is accompanied by radiation of shorter wave-length. This is attributed to a moderated combustion being succeeded by a more vigorous combustion. In the later stages of the combustion period, combustion proceeds more violently, as is evidenced by a rapid rise in pressure, and in this period the ratio of infra-red radiation transmitted through quartz (up to 3.5μ) to that transmitted through fluorite (up to 11.0μ) is 0.55 for a 15% coal-gas mixture, 0.52 for a 12½% mixture, and 0.46 for a 10% mixture. These results show that the more vigorous the combustion the greater the proportion of short infra-red radiation emitted and therefore the greater the proportion of energy acquired during this period by the vibratory degrees of freedom corresponding with the short

wave-length radiation relatively to that acquired by those degrees corresponding with radiation of greater wave-length.

J. F. S.

The Limiting Pressure of Autoxidation. W. P. JORISSEN (*Rec. trav. chim.*, 1921, 40, 539—541; cf. A., 1919, ii, 62; this vol., ii, 99).—A critical review of the conclusions drawn by Weiser and Garrison (this vol., ii, 248) in which it is pointed out that as Centnerszwer (A., 1913, ii, 1052) has shown that phosphorus volatilises into pure oxygen at ordinary pressures, the explanation of the limiting pressure put forward by these investigators is not valid. An alternative interpretation of their seventh experiment is given, which is consistent with the author's conception of limiting pressure.

H. J. E.

The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Solutions containing Sucrose. GEORGE JOSEPH BURROWS (T., 1921, 119, 1798—1802).

Catalysis [of the Decomposition] of Hydrogen Peroxide by Colloidal Manganese Dioxide. A. LOTTERMOSER and R. LEHMANN (*Kolloid Zeitsch.*, 1921, 29, 250—260).—The velocity of decomposition of hydrogen peroxide by colloidal manganese dioxide in the presence of a number of neutral salts and bases has been examined at 30°. The manganese dioxide was prepared in the hydrogen peroxide solution by the action of an alkali hydroxide on potassium permanganate. It is shown that the reaction is very sensitive to accidental impurities, and also that the velocity depends on the order in which the reagents are added to the water in which the reaction takes place. In the present experiments, the reagents were added in the order: hydrogen peroxide, potassium permanganate, alkali. The electrolyte the influence of which is being studied was always added to the water before the reacting substances. The assumption that the increase in the velocity constants is to be explained by the formation and subsequent decomposition of a hydrogen peroxide salt could not be confirmed. The influence of the cations of the added salts, which all have the same anion, follows the lyotrope series $Ba^{++} > Sr^{++} > Ca^{++} > Na^{+} > K^{+} > Li^{+}$, in which Ba^{++} accelerates the reaction to the greatest extent and Li^{+} retards it the most. At higher concentrations, barium falls after calc.um. Mg^{++} and NH_4^{+} , on account of the reduction of the hydroxyl ion which they produce, strongly retard the reaction.

J. F. S.

Catalytic Hydrogenation of Organic Compounds by Base Metals at the Atmospheric Temperature. V. Influence of the Nature and Position of the Halogens in Organic Haloid Compounds on the Removal of Halogen by Catalytic Hydrogenation. C. KELBER (*Ber.*, 1921, 54, [B], 2255—2260).—The rate of absorption of hydrogen by a solution of a gram-millimol of the substance in an excess of aqueous potassium hydroxide

solution in the presence of 3 grams of nickel catalyst has been examined in the cases of chloro-, bromo-, or iodo-acetic acids, phenylchloroacetic, phenylbromoacetic, α -bromopropionic, *o*-, *m*-, and *p*-chloro-, bromo-, and iodo-benzoic acids, *o*-, *m*-, and *p*-chlorophenol, *o*- and *p*-bromophenol, *p*-iodophenol, and the chloro-cresols. The rate of removal of the halogen by catalysis increases with increasing atomic weight of the halogen, and is in general more readily effected with aromatic than with aliphatic compounds. The distinction between the two classes of compound is less obvious with increasing atomic weight of the halogen. In aromatic compounds in which a second substituent is present, the halogen atom in the ortho-position is least readily and that in the para-position most easily replaced by hydrogen. H. W.

Formation of Elements and Structure of the Atomic Nucleus. EMIL KOHLWEILER (*Physikal. Zeitsch.*, 1921, 22, 243—246).—A theoretical paper in which, on the basis of the hypothesis previously put forward by the author (A., 1920, ii, 610, 615, 744), and certain emendations necessitated by the recent work of Aston and Rutherford, the author draws up tables of the possible isotopes of many of the elements up to chromium. The atomic mass of the various elements is calculated and found generally to agree well with the accepted experimental values. J. F. S.

The Structure of the Static Atom. IRVING LANGMUIR (*Science*, 1921, 53, 290—293).—Mathematical. Stability is obtained by the assumption of a repulsive force $Fq = (nh/2\pi)^2 [(1/m) + (1/M)]/r^3$ between an electron of charge e and mass m , and a nucleus of charge Ze and mass M , where n is an integer denoting the quantum state of the electron. The important consequences of Bohr's theory all follow from this one also, and the present theory is much simpler when applied to polyelectronic arrangements.

CHEMICAL ABSTRACTS.

The Structure of the Helium Atom. IRVING LANGMUIR (*Physical Rev.*, 1921, 17, 339—353; cf. A., 1920, ii, 656).—Besides the semi-circular model of the helium atom developed in the paper referred to, the author here develops a double circle model in which the two electrons move in two separate, parallel, circular orbits. This model, however, is unstable, and the ionising potential, computed by applying the quantum theory, is negative. Moreover, the magnetic moment is not zero. The behaviour of the semi-circular model is analysed in greater detail than in the preceding paper. In the case of coupled electrons the quantum theory should be applied, not to the momentum of the individual electrons according to the relation $\oint p dq = h/2\pi$, but rather to the momentum which, by being relayed from one electron to another, passes in each direction around the nucleus.

CHEMICAL ABSTRACTS.

The Dimensions of Atoms and Molecules. W. L. BRAGG and H. BELL (*Nature*, 1921, 107, 107).—When estimates are made

from crystal data and from viscosity data of the diameters of the outer electron shell of the inert gases, the results do not show numerical agreement, but the difference between the two estimates is almost constant; that is, the increase in the size of the atom as each successive electron shell is added is nearly the same (except in the case of neon), whether measured by viscosity or by crystal data. It is indicated that (a) the elements at the end of any one period in the periodic table are very nearly identical as regards the diameters of their outer electron shells, and (b) in passing from one period to the next there is a definite increase in the dimensions of the outer electron shell. Measurements of the infra-red absorption spectra of hydrogen fluoride, hydrogen chloride, and hydrogen bromide lead to the same conclusions. It appears that the forces binding the atoms together are localised at that part of the electron shell where linking takes place.

A. A. E.

Molecular Structure and Energy. J. R. PARTINGTON (*Nature*, 1921, 107, 172).—The models postulated by Lewis and Langmuir, and supported by Rankine's viscosity data, for the molecules of certain halogens, nitrogen, nitrous oxide, nitric oxide, and carbon dioxide, are not in agreement with the specific heats of these gases.

A. A. E.

Molecular Structure and Energy. A. O. RANKINE (*Nature*, 1921, 107, 203; cf. preceding abstract).—A criticism of Partington's views on the apparent discrepancy between Lewis's and Langmuir's models and specific heat measurements. Even if the necessity for revising earlier ideas of energy partition on the basis of the quantum theory is entirely left out of account, it is pointed out that the nitrogen molecule is not spherically symmetrical in the same sense as are the atoms of the inert gases, there being two separate massive nuclei instead of one. Further, it is suggested that the nuclei of all polyatomic molecules may be capable of vibration to and fro.

A. A. E.

Isotopes: their Number and Classification. WILLIAM D. HARKINS (*Nature*, 1921, 107, 202—203; cf. this vol., ii, 445, 582).—The author's theory of nuclear building is supported by the observation that elements of even atomic number consist of more than twice as many isotopes as elements of odd atomic number. In nearly all atoms the number of positive electrons and the number of negative electrons are even, whilst the atomic number is even in 89% of the atoms in the surface of the earth and in 98% of those in meteorites. Most atom nuclei have the formula $(p_e)^n$, where M is an even number. It is proposed to classify atoms according to their isotopic number, n , which when added to twice the atomic number gives the atomic weight. The value n may be defined as the number of neutrons (pe) which would have to be added to the atom of the same atomic number, but of zero isotopic number, to give the composition of the nucleus. Thus the formula of any nucleus would be $(p_e)_M(pe)_n$. The isotopic numbers of

elements of even atomic number are mostly even, whilst those of odd atomic number are mostly odd. Graphs showing the relation between the isotopic numbers of elements and their abundance in the earth's crust or in meteorites exhibit well-defined, almost identical, maxima and minima.

A. A. E.

Alteration of the Basis of the Atomic Weights and Decennial Revision of the Atomic Weight Table. G. ODDO (*Gazzetta*, 1921, 51, ii, 161—168).—The history of the controversy concerning the use of the H=1 or the O=16 basis for the calculation of the atomic weights of the elements is outlined, and it is pointed out that the values for the ratio O:H obtained by Stas (15.84—15.88), Keiser (1887), Cooke and Richards, Rayleigh (1889 and 1892), Noyes (1889), Dittmar and Henderson, Morley, Ledue, Thomsen, Berthelot, Keiser (1898), Rayleigh (1904), Guye and Mallet and Noyes (1908) lie between the limits 15.87 and 15.89. Since the value of this ratio is so accurately known, the author suggests that the use of atomic weights referred to the basis O=16 be abandoned. Arguments are also advanced against frequent revision of the atomic weights and the plea made that such revision be effected at ten-year intervals from the present year.

T. H. P.

The New International Commission on Chemical Elements. BOHUSLAV BRAUNER (*Chem. News*, 1921, 123, 230—232).—The author recommends to the New International Commission that the term "atomic masses" be used only for the whole numbers of the isotopes *B* as determined by the physical (Aston's) method, and that the term "atomic weights" be applied to the numbers obtained by chemical methods, no distinction being made between pure elements, mixtures of isotopes, or single isotopes. He also proposes to call the sub-committee of the "International Commission on Chemical Elements" a "Sub-Committee for Atomic Weights."

W. P. S.

Valency and Co-ordination. SAMUEL HENRY CLIFFORD BRIGGS (*T.*, 1921, 119, 1876—1879).

Lecture Experiments on the Kinetics of Reactions in Solutions (Applied to the Landolt Reaction). J. EGGER and B. SCHARNOW (*Ber.*, 1921, 54, [B], 2521—2525).—The authors describe a series of eleven experiments on the reaction expressed by Landolt as the equations: $\text{IO}_3' + 3\text{SO}_3'' = \text{I}' + 3\text{SO}_4''$, $\text{IO}_3' + 5\text{I}' + 6\text{H}' - 3\text{I}_2 + 3\text{H}_2\text{O}$ and $3\text{I}_2 + 3\text{SO}_3'' + 3\text{H}_2\text{O} = 6\text{I}' + 6\text{H}' + 3\text{SO}_4''$. The results obtained demonstrate the characteristic properties of the kinetics of coupled reactions with reference to the influence of the concentration of the components and to the action of catalysts.

T. H. P.

Inorganic Chemistry.

Preparation of Hydrogen by the Partial Liquefaction of Water-gas. GEORGES CLAUDE (*Compt. rend.*, 1921, 173, 653—655).—Previous experiments for the preparation from water-gas of hydrogen for use in the synthesis of ammonia had to be abandoned in 1908 owing to difficulties (cf. *Ibid.*, 1921, 172, 974) that have now been overcome by certain simple devices. The water-gas from which a portion of the carbon monoxide has been removed by preliminary cooling is allowed to expand whilst doing external work and lubrication difficulties due to the low temperatures are overcome by the addition of 5% of nitrogen. In this way, it is easily possible, working on a large scale, to obtain a steady supply of hydrogen containing only 1.5% of carbon monoxide. [Cf. *J. Soc. Chem. Ind.*, 1921, 810.] W. G.

Negative Hydrogen Ions. ALFONS KLEMENC (*Zeitsch. Elektrochem.*, 1921, 27, 470—474).—A theoretical paper in which the difference of energy between the hydrogen atom (H) and that of the negative hydrogen ion (H') is deduced on the basis of Bohr's atomic model and the assumption that both electrons are in the same orbit. The relationship $H' = H + e + 1/n^2 \cdot 39.4$ Cal. is obtained, from which it follows that the process is endothermic in respect of the electron affinity of the halogen atoms. The theoretical value is then calculated, by making use of the thermochemical data of lithium hydride, the specific heats and energy of dissociation of molecular hydrogen, the energy of ionisation of lithium, and Born's lattice energy. The quantity $H' = H + e + 13 \pm 2.8$ Cal. is obtained, but for perfect agreement the value $n = 2$ must be introduced into the above equation. In view of this, it is stated (with reserve) that both electrons of the hydrogen atoms in lithium hydride must occupy the second Bohr orbit. It is possible that the negative hydrogen ion is formed during the determination of the heat of dissociation of hydrogen by Langmuir's method, but the velocity of the reaction appears to be too small for the energy change, 39.4 Cal. Several equilibrium constants connecting H_2 , H, H', and H' are deduced on the basis of the Nernst equation.

J. F. S.

Magnetochemical Examination of Constitutions in Mineral Chemistry. I. The Sulphur Acids. PAUL PASCAL (*Compt. rend.*, 1921, 173, 712—714).—The author has determined the molecular magnetic susceptibilities of the inorganic oxygenated sulphur compounds, the hydroxylaminesulphonates, the amido-sulphonates, and the organic sulphinic and sulphonic acids, the sulphoxides and sulphones, and from his results has calculated the susceptibilities of the various radicals such as SO_3 , SO_2 , etc. The results furnish further proof of the constitution of sulphuric and

thiosulphuric acids, of the various thionic acids, and indicate that the sulphurous and sulphinic acids must contain the group SO_2 .

W. G.

Stability of Persulphates. K. ELBS and P. NEHER (*Chem. Zeit.*, 1921, 45, 1113—1114).—Sodium, potassium, and ammonium persulphates can be preserved almost unchanged for years if kept dry and protected from sunlight. At ordinary temperatures, aqueous solutions show appreciable decomposition after some days, and with increasing temperature the rate of decomposition rapidly increases and is further accelerated by sunlight. At 100° , decomposition is practically complete in one hour, although the actual velocity varies to a considerable extent with the concentration of the solution, and with the nature of the kation, the sodium salt being somewhat more stable than the potassium and ammonium salts. The addition of sodium sulphate distinctly diminishes the velocity of decomposition, whilst the presence of 5% of sulphuric acid accelerates decomposition five to ten times. As an oxidising agent, sodium persulphate is the most useful salt, and it is often advantageous to diminish the velocity of the reaction, and so prevent loss of available oxygen evolved as gas, by adding about 20% of sodium sulphate (anhydrous) to the solution.

G. F. M.

Effect of Freezing on Colloidal Selenium. A. GUTBIER and F. FLURY [with FR. HEINRICH] (*Kolloid Zeitsch.*, 1921, 29, 161—172).—A number of experiments on the influence of freezing on selenium sols are described. In the case of sols produced by the action of sulphur dioxide on solutions of selenious acid at 60° , it is shown that the destruction produced by freezing is greater the more completely the solutions have been purified by dialysis. The assertion of Lottermoser, that the factor which influences the precipitation of the colloid is not the amount of the reduction of temperature, but the complete solidification of the solution to an ice-like mass, could not be confirmed (A., 1909, ii, 27), for in the present experiments the solutions were completely frozen, but on melting the greater part of the colloid went back into solution. Sols produced as above, but at ordinary temperatures after freezing, yield on melting the typical selenium sols if they have not been kept frozen too long. If the freezing is repeated many times, or if the sol is kept in the frozen condition too long, the colour by transmitted light becomes less intense and the stability of the sol becomes much less, particularly toward an increase in temperature. It is also shown that the nature of the reducing agent employed in the preparation of the sols and the temperature of preparation have a great influence on the stability toward freezing. Sols prepared by reduction with hydrazine at 60° and dialysed are much more sensitive to freezing than similar sols prepared by reduction with sulphur dioxide at ordinary temperatures. The hydrazine sols coagulated irreversibly on cooling even before solidification occurred and a red deposit was formed on the bottom and top of the frozen mass. In the case of the sulphur dioxide

sols, it is shown that the concentration of the undialysed sol has a marked influence on the stability towards a reduction of temperature. The more concentrated sols are more readily destroyed by freezing than the more dilute solutions, and even in these cases it is found that on keeping the sol in the frozen state for some time an inhomogeneity is produced, and a red ring of precipitated selenium is formed at the top and bottom of the frozen mass.

J. F. S.

Viscosity and Molecular Dimensions of Gaseous Ammonia, Phosphine, and Arsine. A. O. RANKINE and C. J. SMITH (*Phil. Mag.*, 1921, [vi], 42, 601—614).—The viscosity of ammonia, phosphine, and arsine has been determined by the method previously described (A., 1910, ii, 829) at various temperatures; similarly, measurements have been made with air for comparative purposes. The following values of the viscosity in C.G.S. units $\times 10^{-4}$ and Sutherland's constant, C , are recorded: air, $\eta_0=1.724$, $\eta_{15}=1.799$, $\eta_{100}=2.191$ and $C=117$; ammonia, $\eta_0=(0.943)$, $\eta_{100}=1.303$, $C=(370)$; phosphine, $\eta_0=1.070$, $\eta_{15}=1.129$, $\eta_{100}=1.450$, $C=290$; arsine, $\eta_0=1.470$, $\eta_{15}=1.552$, $\eta_{100}=1.997$, $C=300$. The bracketed values are calculated from the mean of earlier observations of several investigators. By means of Chapman's formula, the area presented by the molecules for mutual collision has been calculated: this is $A=4\pi\sigma^2$ where σ is the radius of the molecule when treated as an attracting elastic sphere. The collision areas in $\text{cm}^2 \times 10^{-18}$ are found to be: ammonia, 0.640, phosphine, 0.911, and arsine, 0.985. The values previously given for the gases neon, argon, krypton, and xenon (*loc. cit.*) have been corrected for an error which was associated with the earlier work, and the following corrected values are given: neon, $C=69$, $A=\pi\sigma^2=0.417$, $\sigma=2.30$; argon, $C=162$, $A=0.648$, $\sigma=2.87$; krypton, $C=212$, $A=0.757$, $\sigma=3.10$, and xenon, $C=283$, $A=0.915$, and $\sigma=3.41$. J. F. S.

The Electronic Synthesis of Chemical Compounds. I. Formation of Ammonia. EGON HIEDEMANN (*Chem. Zeit.*, 1921, 45, 1073).—By passing a mixture of pure hydrogen and nitrogen through an electron tube, maintaining a tension a few volts above the ionisation tension of both gases, a relatively high yield of ammonia was obtained. A parallel is drawn between photochemistry and electron chemistry, in which light and electrons are the respective activating agents.

E. H. R.

Reaction of Nitrous Acid with Hydrazine and with Azoimide. E. OLIVERI-MANDALÀ (*Gazzetta*, 1921, 51, ii, 201—207; cf. this vol., ii, 346).—The method given for the estimation of nitrous acid by Dey and Sen-Gupta (A., 1911, ii, 822; 1912, ii, 296), who find that a nitrite loses two-thirds of its nitrogen in the elementary state when treated with hydrazine sulphate, is not exact, since the decomposition of hydrazine nitrite in this way is accompanied by secondary reactions varying markedly with variation in the experimental conditions. Highly discordant results have, indeed,

been obtained by different authors who have investigated the decomposition of hydrazine nitrite (Girard and Saporta, A., 1904, ii, 678; Francke, A., 1906, ii, 82; Angeli, A., 1894, ii, 93; Curtius, A., 1893, ii, 372; Dennstedt and Göhlich, A., 1898, ii, 425; Sommer, A., 1913, ii, 952; Sommer and Pincas, A., 1916, ii, 316), and many different interpretations of the reaction have been advanced.

The author's experiments on the interaction of equivalent solutions of potassium nitrite and hydrazine sulphate in an atmosphere of carbon dioxide give the same result at the ordinary temperature as at the boiling point of the solution, the mixed gases evolved consisting of about 10.2–11.7% by vol. of nitrogen and 88.3–89.8% of nitrous oxide; this result is not in agreement with Girard and Saporta's equation (*loc. cit.*). When the proportion of nitrous acid taken is increased, the percentage of nitrogen present in the gases evolved at the boiling point of the liquid increases and, when $\text{N}_2\text{H}_4 : \text{HNO}_2 = 2 : 3, 1 : 2, \text{ and } 2 : 5$, amounts to 41.8, 48.6, and 49.1 respectively. As regards the decomposition in presence of sulphuric acid, a solution containing 0.334, 0.334, and 0.334 gram-mol. per litre of hydrazine, nitrous acid, and sulphuric acid yields a mixture of 80% by volume of nitrous oxide and 20% of nitrogen, whilst with 0.334, 0.668, and 0.334 gram-mol., the percentages of the two gases are 68.1 and 30.9 respectively. These results show that the reaction between hydrazine and a nitrite cannot be used for estimating the latter, the nature of the gases liberated as well as their proportions varying with the conditions.

The author has also studied the action of hydrazine hydrate on free nitrous acid under diverse conditions, but in no case was it found possible to detect the formation of hyponitrous acid.

To the two principal reactions given by Sommer and Pincas (*loc. cit.*), it seems probable that there should be added that expressed by the equation $\text{N}_2\text{H}_4 + 2\text{HNO}_2 = \text{N}_2 + \text{N}_2\text{O} + 3\text{H}_2\text{O}$.

T. H. P.

Oxidation and Luminescence of Phosphorus. III. Catalytic Action of Vapours. HARRY B. WEISER and ALLEN GARRISON (*J. Physical Chem.*, 1921, 25, 473–490; cf. this vol., ii, 248, 637).—The vapours of a number of organic compounds influence the rate of oxidation of phosphorus. Most of the vapours examined retard the oxidation, but nitrobenzene and diphenylamine accelerate it. Phosphorous oxide is an intermediate product in the oxidation of phosphorus to phosphoric oxide. The rapid oxidation of phosphorus to phosphorous oxide occurs at 27° in pure oxygen under 1 atm. pressure, whilst that of phosphorous oxide to phosphoric oxide under the same conditions occurs at 63°. As a rule, the heat of reaction of the first step raises the temperature in the reaction zone to the point where the lower oxide oxidises with sufficient velocity to emit light. In a stream of oxygen at temperatures below 27°, the small amount of phosphorus which vaporises is oxidised to phosphorous oxide, and this is slowly converted into phosphoric oxide without the emission of

light. In a stream of gas or vapour containing oxygen, the chief oxidation product is phosphorous oxide if the temperature is low, if the concentration of oxygen in the reaction zone is low, or if the vapours condense on the surface of the phosphorous oxide particles. The ions formed during the oxidation of phosphorus consist of oxide particles about charged nuclei and vapours are adsorbed or condensed both on the charged and uncharged particles. Condensed vapours decrease the conductivity of "phosphorised" air by weighting down the charged particles. If the adsorbed vapours react with phosphorous oxide they increase the velocity of oxidation of phosphorus both by removing oxide particles from the zone of reaction and by raising the temperature. Nitrobenzene and diphenylamine act in this way. If the adsorbed vapours are inert they prevent further oxidation of phosphorous oxide and also form a cloud near the surface of the phosphorus which retards the action. If two vapours are adsorbed to the same extent, the heavier one will form the denser cloud and will have the greater inhibiting action. It is concluded that vapours (with the exception of a trace of water vapour) which influence the rate of oxidation of phosphorus are not catalysts in the ordinary sense of the word. The vapours are merely condensed on the charged or uncharged products, and act as described above. The cloud surrounding the phosphorus approaches nearer the surface as the oxidation becomes less energetic, and may form a protecting film which reduces vapourisation and oxidation of the phosphorus to a minimum.

J. F. S.

Fusion of Carbon. EUGEN RYSCHKEWITSCH (*Zeitsch. Elektrochem.*, 1921, 27, 445—452; cf. this vol., ii, 258, 586).—A description of further experiments on the fusion of carbon. It is shown that carbon can be melted under ordinary pressure by an electric current. The carbon always melts at the point where the current and consequently the temperature is the highest. Under suitable conditions, high current efficiency, and good heat insulation, carbon may be melted by comparatively small currents. The solidified drops of carbon and the two points from which the drop has fallen consist of pure graphite. The sublimation point of carbon at ordinary pressures lies very near to the melting point, and in consequence the failures to melt carbon described in the literature are to be attributed to the superposition of the sublimation over the melting. In saturated carbon vapour, unusually large and well-formed graphite crystals are produced, which grow in the planes of stronger affinity. The completely closed furnaces used in the melting of carbon have made a determination of the melting point impossible up to the present.

J. F. S.

Viscosities and Molecular Dimensions of Methane, Hydrogen Sulphide, and Cyanogen. A. O. RANKINE and C. J. SMITH (*Phil. Mag.*, 1921, [vi], 42, 615—620; cf. this vol., ii, 694).—The viscosities of methane, hydrogen sulphide, and cyanogen have been measured at 17° and 100°, and from the results the values of the Sutherland constant (C) and the collision area in $\text{cm}^2 \times 10^{-16}$

(\bar{A}) have been calculated. The following values are recorded: methane, $\eta_0=1.035$, $\eta_{17}=1.094$, $\eta_{100}=1.363$, $C=198$, and $\bar{A}=0.772$; hydrogen sulphide, $\eta_0=1.175$, $\eta_{17}=1.251$, $\eta_{100}=1.610$, $C=331$, and $\bar{A}=0.773$; cyanogen, $\eta_0=0.935$, $\eta_{17}=0.995$, $\eta_{100}=1.281$, $C=330$, and $\bar{A}=1.21$. The viscosity values are given in C.G.S. units $\times 10^{-4}$.
J. F. S.

Helium-bearing Natural Gas. G. SHERRBURNE ROGERS (*U.S. Geol. Survey, Prof. Paper*, 1921, No. 121, 113 pp.).—A résumé of the chemistry of helium and the radioactive elements, and a detailed account of the distribution, chemical composition, and chief sources of helium-bearing natural gas. Helium constitutes from 0.5 to 2% of certain nitrogen-rich natural gases occurring in Kansas, whilst natural gas occurring in Europe contains a maximum of only 0.33% helium. [See *J. Soc. Chem. Ind.*, 1921, Dec.]
J. S. G. T.

Some Properties of Fused Sodium Hydroxide. THOMAS WALLACE and ALEXANDER FLECK (*T.*, 1921, 119, 1839—1860).

Conversion of Ammonium Sulphide and of Thiosulphates into Sulphates. W. GLUUD (*Ber.*, 1921, 54, [B], 2425—2426).—At 100°, ammonium sulphide in aqueous solution may be readily and completely converted into ammonium sulphate by air under a pressure of 10 atmospheres. Under similar conditions, sodium thiosulphate undergoes total transformation into sulphate, provided that sufficient alkali is present to unite with the sulphuric acid formed from the sulphur; if such excess of alkali is lacking, part of the sulphur separates in the elementary condition. A lower pressure than that mentioned above may be used, but in such case either the temperature must be raised or the duration of the action increased.
T. H. P.

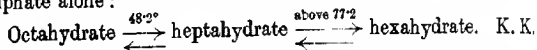
The Melting and Boiling Points of Ammonium Sulphate. ERNST JÄNECKE (*Zeitsch. angew. Chem.*, 1921, 34, 542—543; cf. A., 1920, ii, 757).—The equilibrium between ammonia, ammonium sulphate, ammonium hydrogen sulphate, sulphuric acid, and water has been further investigated and the results are shown graphically. Ammonium sulphate when heated evolves more ammonia than water, so that a certain amount of ammonium hydrogen sulphate (m. p. 147°) is first formed, and later this loses water, giving the pyrosulphate. The equilibrium diagram is also augmented by the inclusion of an acid sulphate, $\text{NH}_4\cdot\text{H}_2(\text{SO}_4)_2$ (m. p. 48°), and an ammonia compound $(\text{NH}_4)_2\text{SO}_4\cdot 2\text{NH}_3$. There are eutectics between sulphuric acid and the acid sulphate (m. p. -20°), between the acid sulphate and the hydrogen sulphate (m. p. 39°), and between the latter and the pyrosulphate (m. p. 138°).
A. R. P.

The Graphitic Nature of the Carbon of Nitro-lime. NAOTO KAMEYAMA (*J. Chem. Ind. Japan*, 1921, 24, 1131—1142).—It is found that the carbon which separates when nitro-lime is treated with concentrated hydrochloric acid and 55% hydrofluoric acid is
VOL. CXX, ii.

entirely graphitic. This was proved by the specific gravity (2.246), the heat of combustion (7,857 cal. per gram), the diffraction rings formed by X-rays, the electrical conductivity and by oxidation to graphitic acid, satisfactory coincidence being obtained in parallel experiments with Acheson graphite.

K. K.

The Octahydrate of Magnesium Sulphate. SHIRÔ TAKEGAMI (*J. Chem. Soc. Japan*, 1921, 42, 441—453; cf. this vol., ii, 30).—The equilibrium systems of magnesium sulphate, sodium sulphate, and water at 25° and 30° were studied, and the existence of the octahydrate of magnesium sulphate was proved. (From these results it is deduced that in the equilibria of the reciprocal salt pairs, sodium chloride and magnesium sulphate and sodium sulphate and magnesium chloride at 25° there are ten solid phases, not nine as previously stated (*loc. cit.*), the phase $\text{MgSO}_4 \cdot 8\text{H}_2\text{O}$ having to be added although its numerical values are still lacking.) The solid phase (der Bodenkörper) of the system at 25° is always the octahydrate. At 30°, also when the solution contains less than 32% of sodium sulphate, the solid phase is the octahydrate, which, however, is replaced by the heptahydrate when the concentration of the sodium sulphate exceeds 32%. When the solution contains about 7—9% of sodium sulphate, the solid phase below 45.5° is the octahydrate, whilst between 46.1° and 77.2° it is the heptahydrate. From the transition point in the presence of sodium sulphate, the following points are deduced for the case of magnesium sulphate alone:



The Atomic Volume of Isotopes. FREDERICK SODDY (*Nature*, 1921, 107, 41—42).—Values obtained for the density and atomic weight of ordinary lead, lead from thorite, and lead from uranium minerals have been compared. It is concluded that the atomic volumes cannot differ by so much as three parts in ten thousand and the atomic diameters by so much as one part in ten thousand.

A. A. E.

The Purification of Mercury. C. HARRIES [and FRITZ EVERS] (*Zeitsch. angew. Chem.*, 1921, 34, 541—542).—In order to test the value of the method described previously (this vol., ii, 552) for the purification of mercury, comparative tests on a 1% lead amalgam were carried out. One portion was allowed to fall twice through a long column of nitric acid (d 1.175); the resulting product contained no trace of lead, but the loss of mercury was 3.7%. A second portion was heated for ten hours at 150—160° while passing a current of air through it; the resultant metal was left for several hours in contact with strong hydrochloric acid, and, after thorough washing with water, was found to be free from lead. The loss of mercury in the latter case was only 2%. An amalgam containing 1% of tin after three passages through nitric acid lost 9.2% of its mercury content and the remaining metal still contained traces of tin. Treated by the hot air method, it

lost only 1.4% of mercury in fifteen hours, but the residual metal contained some tin. A second test showed that if the air used is first passed through fuming hydrochloric acid all the tin is removed in twelve hours.

A. R. P.

Critical Constants of Mercury. SOPHUS WEBER (*Onnes Comm. Leiden Suppl.*, 1920, 21—31; from *Chem. Zentr.*, 1921, iii, 769—770).—Observation on the critical temperature of mercury showed that it is higher than formerly supposed and probably exceeds 1700° Abs. From a consideration of the data of Bender on the densities of liquid and vaporous mercury, the author shows that the critical temperature must be about 1450+273° Abs. On this assumption, the critical density, d_c , is 5.0 and the critical pressure, p_c , about 1042 atmospheres, which values are in good agreement with those obtained by extrapolation by Knudsen's formula. Plotting d/d_c against T/T_c and $\log p_c/p$ against $(T_c/T-1)$, mercury is shown to fall into line with other monatomic gases.

G. W. R.

Double Nitrate of Aluminium and Potassium. N. M. LA PORTE (U.S. Pat. 1377081).—A double nitrate of aluminium and potassium of the formula $\text{Al}(\text{NO}_3)_3 \cdot 3\text{KNO}_3 \cdot 10\text{H}_2\text{O}$ is prepared by crystallisation from a solution of potassium nitrate and aluminium nitrate in nitric acid. The proportions of the potassium nitrate and aluminium nitrate may be somewhat varied.

CHEMICAL ABSTRACTS.

Graphitisation in Iron-Carbon Alloys. KÔTARÔ HONDA and TAKEJIRO MURAKAMI (*Sci. Rep. Tohoku Imp. Univ.*, 1921, 10, 273—303).—Graphitisation occurs in iron-carbon alloys as a decomposition of cementite and not as a separation of graphite in the molten state. The decomposition is effected catalytically by carbon monoxide or dioxide according to the equations $2\text{CO} = \text{CO}_2 + \text{C}$ and $\text{CO}_2 + \text{Fe}_3\text{C} = 2\text{CO} + 3\text{Fe}$. The process continues until the concentration of the gas in the alloy is reduced below a certain amount or until the temperature falls below the graphitising range. Any treatment of the alloy tending to eliminate carbon dioxide or monoxide present, such as heating above 1400°, will also prevent graphitisation. The formation of flaky graphite is explained by the aggregation of graphite particles as they separate from cementite by reason of interfacial tension. A phase diagram of the system iron-carbon is given embodying the authors' theories.

G. W. R.

The Preparation of Nickel Carbonyl. E. TASSILLY, H. PÉNAU, and E. ROUX (*Bull. Soc. chim.*, 1921, [iv], 29, 862—864).—In the preparation of nickel carbonyl by passing carbon monoxide over reduced nickel the optimum temperature is 45° at a pressure of 3 cm. Within reasonable limits, the yield of carbonyl from carbon monoxide was independent of the rate of flow of the gas, provided that the velocity was not so great as to prevent condensation by suitable cooling. The coefficient of utilisation was 84% for the metal and 37% for the gas.

W. G.

Physico-chemical Analysis of Zirconium Oxychlorides and Zirconium Oxide Sols. MONA ADOLF and WOLFGANG PAULI (*Kolloid Zeitsch.*, 1921, 29, 173—184; cf. A., 1917, ii, 563).—The complex ionisation of zirconium oxychloride has been examined from experimental data on the hydrogen- and chlorine-ion concentrations, the total zirconium and chlorine concentrations of the solution, the electrical conductivity at 25°, the depression of the freezing point, and the electric migration. The solutions used were made in cold water and kept for ten days before use. The ionisation occurs according to the scheme (i) $\text{ZrAn}_4 + 4\text{H}_2\text{O} \rightleftharpoons \text{Zr}(\text{OH})_4 + 4\text{HAN}$, (ii) $2\text{ZrAn}_4 \rightleftharpoons \text{ZrAn}_4\text{ZrAn}_2^{''} + 2\text{An}'$, (iii) $2\text{ZrAn}_4 \rightleftharpoons \text{ZrAn}_6^{''} + \text{ZrAn}_2^{''}$ (An—an univalent anion). The results show that the ratio between the zirconium hydroxide formed and the unhydrolysed oxychloride is simple and can be expressed in different concentrations by the figures 1:1, 3:4, 2:3, and 1:2. A comparison of the hydrolysis with a normal hydrolysis shows that an astonishingly large amount of zirconium hydroxide is formed and a very high degree of hydrolysis is attained. The hydrolysis is not only abnormal in respect of its high value, but also in its connexion with the concentration of the hydrochloric acid. It does not increase with successive dilution, but fluctuates irregularly. It fluctuates between 35% and 49% for a dilution of 500 times. This behaviour is attributed to the formation of complexes, of the type $x\text{Zr}(\text{OH})_{4/3}\text{ZrOCl}_2$, which react with the hydrochloric acid and form highly complex acids of the types $\text{Zr}(\text{OH})_4\text{Cl}_2\text{H}_2$ and $\text{Zr}(\text{OH})_2\text{Cl}_4\text{H}_2$. Curves representing the change in concentration of the hydrogen and chlorine ions respectively present an unique phenomenon, inasmuch as they intersect three times with changing concentration. The points of intersection lie approximately at $N/100$, $N/8$, and $3N/8$. Transport measurements show that the nature of the ion containing zirconium changes in the regions between the intersections of the curves. Tables of the complexes present and the ions to which they give rise are included in the paper. Zirconium oxide sols, produced by the dialysis of solutions of the oxychloride, have been examined. The sols are coagulated by electrolytes only in concentrated solutions ($N/4$ and above). Two of the sols have been investigated and shown to have the composition (a) $5\text{Zr}(\text{OH})_4\text{ZrOCl}_2$, and (b), $7\text{Zr}(\text{OH})_4\text{ZrOCl}_2$.

J. F. S.

Mineralogical Chemistry.

Crystal Structure of Alabandite (MnS). RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1921, [v], 2, 239—249).—The various possible space-groups suggested by the measurements of the X-ray reflections from a cube-face and also from the powdered mineral are discussed. The arrangement of the atoms (with either four

or thirty-two chemical molecules to the unit cell) is either that of the "rock-salt type" or a grouping (tetrahedral or tetartohedral) very close to this.

L. J. S.

Dolomite from Binn, Switzerland. PAUL KOLLER (*Jahrb. Min.*, 1918, *Beil.-Bd.* 42, 457—498).—A detailed crystallographic description is given of the colourless water-clear crystals from the saccharoidal dolomite-rock. Crystals of another type from the same occurrence are transparent with a pale yellowish tinge; these have refractive indices $n_o = 1.6799$, $n_e = 1.5013$ (Na), and gave analyses I and II by P. POOTH.

	CaCO ₃ .	MgCO ₃ .	FeCO ₃ .	Sp. gr.
I	53.38	46.45	0.13	2.832
II	53.19	46.52	0.09	—
III	52.35	46.02	1.79	2.837

Both these analyses show a slight excess of magnesia over that required by normal dolomite, I corresponding to $32\text{CaCO}_3, 33\text{MgCO}_3$ and II to $26\text{CaCO}_3, 27\text{MgCO}_3$. Corresponding with the low percentage of iron, the refractive indices are lower than any previously determined for dolomite. Analysis III is of dolomite from Scaleghia, Disentis, corresponding with $\text{FeCO}_3, 36\text{CaCO}_3, 37\text{MgCO}_3$. Etching experiments were made on cleavage flakes with sulphuric, nitric, hydrochloric, acetic, and formic acids, each of which produces different forms of etch-figures. Different forms of etch-figures are also produced by the same acid when of different concentrations. The material of analyses I and II yielded the same type of etch-figures, but the more ferruginous dolomite is rather more readily attacked.

L. J. S.

Lazulite from Graves Mountain, Georgia. THOMAS L. WATSON (*J. Washington Acad. Sci.*, 1921, 11, 386—391).—Analysis, by J. W. WATSON, of material from this well-known locality for lazulite gave:

P ₂ O ₅ .	Al ₂ O ₃ .	FeO.	MgO.	CaO.	H ₂ O.	SiO ₂ .	Total.	Sp. gr.
38.25	33.92	3.99	9.08	3.12	5.83	6.05	100.24	2.958

Deducting silica as quartz, this gives the usual formula $(\text{Fe,Mg,Ca})\text{O}, \text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, \text{H}_2\text{O}$. The calcium is, however, higher than previously recorded for the mineral, and this variety is therefore distinguished as calcium lazulite. Other occurrences of lazulite in the United States are noted.

L. J. S.

Cornetite from Bwana Mkubwa, Northern Rhodesia. A. HUTCHINSON and A. M. MACGREGOR (*Min. Mag.*, 1921, 19, 225—232).—The mineral occurs as a thin, crystalline crust of a fine peacock-blue colour on sandstone and shale. The minute crystals are orthorhombic with the forms $m(110)$, $d(102)$, $v(221)$; $a:b:c = 0.9855:1:0.7591$. Optic axial plane (001), acute negative bisectrix perpendicular to (100). $d\ 4.10$, $H\ 4-5$. Analysis gave:

CuO.	Fe ₂ O ₃ .	P ₂ O ₅ .	H ₂ O.*	Insol.	Total.
67.28	0.53	18.33	8.24	4.03	98.91

* Loss at 190°, 0.18; loss on ignition 8.77%.

This gives the formula $2\text{Cu}_3(\text{PO}_4)_2 \cdot 7\text{Cu}(\text{OH})_2$ or perhaps $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{Cu}(\text{OH})_2$. The mineral agrees in its crystallographic and optical characters with cornetite from Katanga (A., 1920, ii, 441) and differs only in not containing cobalt replacing copper.

L. J. S.

Jurupaite, a New Mineral. ARTHUR S. EAKLE (*Amer. Min.*, 1921, 6, 107—109).—This is another of the several hydrated calcium silicates described from the metamorphic limestone at Crestmore, California (A., 1919, ii, 113). It resembles pectolite in appearance, and occurs in the blue calcite as compact spheres of soft, silky, radiating fibres. The oblique optical extinction suggests monoclinic symmetry. The mineral fuses readily to a clear white glass, and is easily soluble in dilute hydrochloric acid without gelatinisation. It gives no colour with phenolphthalein. The mean of two analyses is:

SiO_2	CaO	MgO	H_2O	Total	Sp. gr.
43.87	38.66	4.19	7.89	99.61	2.75

This gives the ratios $2(\text{Ca}, \text{Mg})\text{O} : 2\text{SiO}_2 : \text{H}_2\text{O}$. The loss of water at 120° is less than 1% and all is not expelled over the bunsen flame. The formula is therefore written $\text{H}_2(\text{Ca}, \text{Mg})_2\text{Si}_2\text{O}_7$, being like crectmoreite and riversideite a derivative of orthosilicic acid. Plazolite (A., 1921, ii, 270) from this locality shows several points of similarity to calcium-garnet.

L. J. S.

The Cerium Minerals of Bastnäs, Sweden. PER GELMER (*Sveriges Geol. Undersökning*, 1921, *Årbok*, 14 (for 1920), No. 8, 1—24).—Cerite, the mineral in which cerium was discovered, is known only from this locality. A detailed description is given of the mode of occurrence of the cerium ore. Examined in thin sections under the microscope, it is seen to consist of a fine grained aggregate of the cerium minerals cerite, bastnäsite, törnebohmit, orthite, fluocerite, and lanthanite, the optical characters of each of which are given. A new estimation of water in the orthite (*d* 4.20) gave 1.52. Introducing this value in Cleve's analysis (1863) the ratios $\text{H}_2\text{O} : \text{RO} : \text{R}_2\text{O}_3 : \text{SiO}_2$ become 1 : 4.29 : 2.61 : 5.93, which is a closer approach to the epidote formula. The new mineral *törnebohmit* was detected in the micro-sections as pale green grains (*d* 4.94) differing in optical characters from the associated cerite. Analysis by R. MAURILIUS gave (also chalcopyrite 0.96, molybdenite not det., insoluble 0.95):

SiO_2	Ce_2O_3	$(\text{La}, \text{Di})_2\text{O}_3$	Al_2O_3	FeO	MnO	MgO	CaO	F	Ign.	Total
22.05	27.52	34.85	8.55	1.91	0.05	0.49	0.23	0.29	1.70	99.55

Calculating RO as R_2O_3 , these results give a formula, $\text{R}_2(\text{ROH})(\text{SiO}_2)_2$, analogous to those of andalusite and topaz. The mineral is, however, more closely allied to cerite, from which it differs chemically in containing more aluminium and less calcium.

L. J. S.

Monticellite Crystals from a Steel-works Mixer Slag. A. F. HALIMOND, with analysis by J. H. WHITELEY (*Min. Mag.*, 1921, 19, 193—195).—The pale-brown, transparent crystals are

orthorhombic with the forms $b(010)$, $m(110)$, and $k(021)$; $a:b:c=0.4382:1:0.5779$. The optic axial plane is parallel to (001) and the acute negative bisectrix perpendicular to (010) ; α 1.663, β 1.674, γ 1.680; $2V$ $74\frac{1}{2}^\circ$, d 3.20. Analysis shows the presence of 16.5 mol. % of true olivine in solid solution with the monticellite $\text{Ca}(\text{Mg}, \text{Fe}, \text{Mn})\text{SiO}_4$, which is in accord with the variation in the physical characters from those of pure monticellite.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	P_2O_5	CaS	Total
34.80	0.24	0.27	trace	4.11	13.39	17.65	28.45	0.905	0.055	69.87

L. J. S.

Chemical Constitution of Zeolites. G. TSCHERMAK (*Sitzungsber. Akad. Wiss. Wien*, 1917, 126, 541—606, 1918, 127, 177—189; from *Jahrb. Min.*, 1921, ii, Ref. 150—153).—Twenty-one new analyses are given of various zeolites. In all cases the ratio $\text{Al}:\text{Ca}(\text{Sr}, \text{Ba})+\text{Na}_2(\text{K}_2)$ is 2:1. Omitting oxygen, all zeolites may be represented by the formulæ $\text{Si}_x\text{Al}_2\text{CaH}_y$ and $\text{Si}_x\text{Al}_2\text{Na}_z\text{H}_v$, where x and z range from 2 to 10, and y and v from 2 to 9. Or gain, neglecting hydrogen, they all contain a group $\text{Si}_x\text{Al}_2\text{CaO}_8$ or $\text{Si}_x\text{Al}_2\text{Na}_2\text{O}_8$. This group is regarded as a nucleus ("Kern") and represented as Kc or Kn respectively (also Kb and Ks for the corresponding barium and strontium nuclei). The various zeolites are regarded as compounds of one or other of these nuclei with a silicic acid, combined water, and water of crystallisation. The silicic acid and water of hydration are supposed to form a network enclosing the nuclei. Such a structure is regarded as offering an explanation of the variation of the optical characters of the zeolites with loss or gain of water, the various adsorption phenomena, and the ease with which the bases may be replaced. The following is a summary of the different groups:

A. Orthosilicates in combination with SiH_4 and H_2O : Natrolite, $\text{SiH}_4Kn=\text{Si}_3\text{Al}_2\text{Na}_2\text{H}_4\text{O}_{12}$. Scolecite, $\text{SiH}_4Kc\text{OH}_2=\text{Si}_3\text{Al}_2\text{CaH}_8\text{O}_{13}$. Mesolite, a double salt of these two in the ratio 1:2. Edingtonite, $\text{SiH}_4Kb\text{OH}_2\text{aq}=\text{Si}_3\text{Al}_2\text{BaH}_8\text{O}_{14}$. Gismondine, $\text{H}_2\text{OKcO}_2\text{H}_4\text{aq}=\text{Si}_3\text{Al}_2\text{CaH}_8\text{O}_{12}$, also with SiH_4 in place of H_2O . Laumontite, $\text{SiH}_4Kc\text{SiH}_2=\text{Si}_4\text{Al}_2\text{CaH}_8\text{O}_{16}$. Thomsonite, a double salt of the compounds $\text{H}_2\text{OKnOH}_2\text{aq}$ and H_2OKcOH_2 in the ratio 1:3; also in the latter SiH_4 in place of H_2O .

B. Disilicates combined with polysilicic acids and H_2O : Analcite, $\text{Si}_2\text{H}_4Kn=\text{Si}_4\text{Al}_2\text{Na}_2\text{H}_4\text{O}_{12}$, also with Si_4H_8 , Si_4H_6 , or H_2O in place of Si_2H_4 . Faujasite, $\text{Si}_4\text{H}_8Kc\text{O}_2\text{H}_4\text{aq}$, also with Si_2H_4 . Chabazite, $\text{Si}_4\text{H}_8Kc\text{O}_2\text{H}_4\text{aq}=\text{Si}_4\text{Al}_2\text{CaH}_{12}\text{O}_{18}$, also with Si_4H_8 , Si_2H_2 , or SiH_4 . Gmelinite with Kn in place of Kc . Levyne like chabazite with Si_2H_2 and SiH_2 . Stilbite, $\text{Si}_4\text{H}_8Kc\text{OH}_2\text{aq}=\text{Si}_5\text{Al}_2\text{CaH}_{14}\text{O}_{23}$, also with Si_6H_{12} , Si_4H_4 , or Si_2H_4 . Harmotome with Kb instead of Kc . Phillipsite like stilbite but with Si_2H_4 , Si_2H_2 , SiH_4 , SiH_2 . Heulandite, $\text{Si}_4\text{H}_8Kc\text{O}_2\text{H}_4\text{aq}=\text{Si}_4\text{Al}_2\text{CaH}_{10}\text{O}_{21}$, also with Si_6H_6 , Si_4H_8 , or Si_2H_4 . Brewsterite with Ks in place of Kc . Mordenite like heulandite with Si_2H_8 .

L. J. S.

Ferroanthophyllite from Idaho. EARL V. SHANNON (*Proc U.S. Nat. Museum*, 1921, 59, 397—401).—A greyish-green, asbesti-

form mineral intergrown with galena occurs in the Tamarack-Custer mine near Gem in the Coeur d'Alene district. It is orthorhombic with optically positive elongation, $\alpha=1.668$, $\gamma=1.685$; $d\ 3.24$. It is insoluble in acids, and fuses to a black, magnetic glass. Analysis gave:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	CaO	MgO	H ₂ O(<110°)	H ₂ O(>110°)	Total
49.30	1.30	2.15	30.50	3.48	10.73	0.66	0.18	2.13	100.43

Deducting ferric oxide and alumina as gedrite (RO.R₂O₂.SiO₂), this gives the metasilicate formula (Fe,Ca,H₂,Mn)O₂.SiO₂, but only when the water, which is expelled at a high temperature, is taken into account. Being the iron end-member of the anthophyllite series the name ferroanthophyllite is applied [cf. iron-anthophyllite, A., 1919, ii, 165]; similarly, the magnesium end-member of this series may be called magnesiananthophyllite. L. J. S.

A New Type of Mineral Water: Nitrated Waters. CHARLES LEPIERRE (*Compt. rend.*, 1921, 173, 783—786).—A mineral water found at Ericeira in Portugal, obtained from a well 15 metres deep and 50 metres from the sea, contained 0.686 gram of nitrates, expressed as sodium and calcium nitrates, per litre, equivalent to 18.8% of the total mineral salts. Their origins are considered to be due to biochemical and hydrological phenomena. W. G.

Analytical Chemistry.

Apparatus for Technical Gas Analysis. G. ANDOYER (*Ann. Chim. anal.*, 1921, 3, 293—294).—The apparatus consists of a measuring burette provided with a water-jacket; the bottom of the burette is connected with a levelling reservoir, whilst the top is fitted with a three-way tap. The absorption pipettes are connected, in turn, with the stem of the tap and thence with the burette; the other branch of the three-way tap carries a small funnel by which water may be introduced for washing out reagents. W. P. S.

Atmospheric Corrections for the Harcourt Standard Pentane Lamp. E. B. ROSA, E. C. CRITTENDEN, and A. H. TAYLOR (*J. Opt. Soc. Amer.*, 1921, 5, [v], 444—452).—A review of results obtained for the factor correcting the candle-power of the Harcourt 10-candle pentane lamp for variations of humidity of the atmosphere. The mean correcting factor determined at the National Physical Laboratory is 0.645, whilst the result obtained at the Bureau of Standards is 0.567, the factor in each case representing the percentage decrease in candle-power due to an increase of 1 litre of water vapour per cub. metre of air. The discrepancy in the two values is traced to a difference of atmospheric temperature in the two cases, and it is shown that the experimental values are

brought into agreement by using two factors, namely, a factor 0.52% decrease in candle-power per litre of water vapour per cub. metre of air (in the absence of any temperature difference) and a factor 0.08% decrease per degree rise of temperature. The factor 0.52% agrees with the recently determined value found at the Bureau of Standards and is in agreement with results obtained recently by Takatsu and Tanaka in Japan. It is suggested that 15° should be taken as the normal atmospheric temperature for calculation of the candle-power of the lamp. J. S. G. T.

Device for Filling Burettes. G. BRUHNS (*Chem. Zeit.*, 1921, 45, 1004).—The lower end of a burette, without a tap, is connected with a short vertical length of glass tube carrying a side tube; this side tube is bent downwards and provided with a jet and spring clip. The end of the vertical tube is connected by a rubber tube with a piece of glass tube which reaches to the bottom of the reservoir containing the reagent solution. The burette is filled by opening a spring clip on the latter piece of rubber tube and applying suction to the top of the burette. W. P. S.

Colorimetric Method of Estimating Hydrogen-ion Concentration. Some Applications in the Analytical Laboratory. NORMAN EVERS (*Analyst*, 1921, 46, 393–400).—The colorimetric method is described in detail; the method depends on the fact that with different indicators the colour change extends over a characteristic zone of hydrogen-ion concentration. The method may be used with clear or turbid liquids free from colour, for coloured liquids, and is useful for ascertaining the reaction of such substances as sodium salicylate, morphine hydrochloride, calcium chloride, potassium iodide, etc. W. P. S.

Methyl-orange as an Indicator in the Presence of Indigo Carmine. FRANK X. MOERK (*Amer. J. Pharm.*, 1921, 93, 675–679; cf. A., 1907, ii, 910).—The sensitiveness of methyl-orange, particularly in slightly coloured solutions, may be increased by the addition of indigo-carmin; 1 gram of methyl-orange and 2 to 4 grams of indigo-carmin per litre of water is a suitable concentration for the indicator solution. W. P. S.

A Simple Method for the Preparation of Sodium Hydroxide Solution free from Carbonate. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, 58, 1413–1417).—Commercial sodium hydroxide is dissolved in water to form an approximately normal solution. To each litre 50 c.c. of milk of lime is added; after well shaking, the solid is allowed to settle and the caustic solution decanted off with the usual precautions. The solution is titrated and diluted to 0.1N; it is quite free from carbonate, and contains only 1–2 mg. of calcium per litre, which has no influence in analytical determinations. S. I. L.

Direct Estimation of Water in Mixed Sulphuric and Nitric Acids. E. BERL and W. VON BOLTENSTERN (*Zeitsch. angew. Chem.*, 1921, 34, 526–528).—A calorimeter for determining the heat of dilution of the sample consists of a vacuum-lined vessel

40 mm. in diameter and 300 mm. high. It is fitted with an agitator consisting of two blades of sheet glass or aluminium connected together and worked by two rods, and with a thermometer graduated to 1/10 of a degree. Two hundred c.c. of distilled water are placed in the calorimeter, 20 c.c. of mixed acid added through a fine glass tube dipping below the surface of the water, and the corrected rise of temperature obtained as with the Mehler bomb calorimeter. The water content of the acid is read off from a curve prepared by a series of tests of different dilutions of an acid of known composition. Different ratios between the two acids correspond with different curves. An increase of 1% in the N_2O_3 content of the acid was also found to give a water figure 1% too high. Organic matter is without effect, and for varying dilutions of a mixture of constant composition determinations can be rapidly made to an accuracy of 0.05–0.06% H_2O . C. I.

A New Process for the Estimation of Fluorine in the Cold. TRAVERS (*Compt. rend.*, 1921, 173, 836–838).—The fluorine is first converted by suitable means into alkali fluoride. To the fluoride solution, generally alkaline, a known amount of silica, as potassium silicate, is added. Usually twice the theoretical amount of silica required to convert the fluorine to potassium silicofluoride is sufficient. The liquid is then neutralised with hydrochloric acid using methyl-orange as an indicator, and an excess of acid, about 2 c.c., is added. Solid potassium chloride is added until the solution contains 20% of it. The precipitate is filtered off, washed free from acid with 20% potassium chloride and titrated with $N/5$ -potassium hydroxide as previously described in the estimation of silica (this vol., ii, 710). One c.c. of $N/5$ -potassium hydroxide is equivalent to 0.0057 gram of fluorine. W. G.

Estimation of Small Quantities of Fluorine in Natural Products by Means of Hempel and Scheffler's Gasometric Method. H. SERTZ (*Zeitsch. anal. Chem.*, 1921, 60, 321–330).—The method described by Hempel and Scheffler (*A.*, 1899, ii, 380) is suitable for the estimation of the small quantities of fluorine occurring in certain vegetable substances; when the ash of the latter contains much carbonate or chloride, a preliminary treatment with 10% acetic acid is recommended. W. P. S.

Some Notes on the Estimation of Sulphur and Chlorine by the Lamp Method. S. BOWMAN (*J. Inst. Petroleum Tech.*, 1921, 7, 334–338).—In estimating sulphur in petroleum products by this method a certain amount of sulphur is always absorbed by the wick. A method of eliminating this source of error is described. [See further *J. Soc. Chem. Ind.*, 1921, Dec.] L. A. C.

Estimation of Sulphate-, Chloride-, and Carbonate-ions in Soda-Lime-Glass. MASAO IKAWA (*J. Chem. Soc. Japan*), 1921, 42, 768–785).—The sulphate and chloride radicles are precipitated as barium sulphate and silver chloride respectively, from the clear solution, obtained by warming on a water-bath the finely-powdered

glass with three times its weight of pure ammonium hydrogen fluoride in presence of acid with constant stirring. The sulphur in the glass is estimated by oxidation with bromine water in the course of the decomposition of a sample with ammonium hydrogen fluoride, followed by precipitation as barium sulphate, the amount of sulphur being calculated from the difference between this and the estimation of the sulphate. For the determination of the carbonate, the sample is decomposed with 30% solution of the fluoride in a lead flask, and the carbon dioxide produced absorbed in soda-lime as in the Fresenius-Classen method.

Finely powdered glass absorbs 0.1260% of carbon dioxide by exposure to the air for eight months, but the absorption during the preparation of the sample for analysis is negligible.

Pure ammonium hydrogen fluoride is prepared by passing silicon fluoride into water and treating the hydrofluorosilicic acid formed with excess of ammonia. The solution is filtered and concentrated in a platinum dish; ammonium hydrogen fluoride crystallises on cooling; it is further purified by sublimation. A 30% solution of ammonium hydrogen fluoride is not decomposed by heating at 90°, but in more concentrated solutions decomposition occurs, a 50% solution evolving hydrogen fluoride, ammonia, and ammonium fluoride at that temperature. K. K.

Rapid Process for Estimating Phosphoric Acid. H. COPEAUX (*Compt. rend.*, 1921, 173, 656—658).—The method is based on the fact that when phosphoric acid in the presence of another acid, such as sulphuric or hydrochloric acid, is shaken with ether and an alkali molybdate the phosphomolybdic acid formed unites with ether and water to give a dense yellow liquid which is not miscible with water. The estimation is conducted in a specially designed graduated tube, which is described. Into the tube is run 10 c.c. of the phosphate solution, 10 c.c. of 20% sulphuric acid, and sufficient ether to give a layer of 3—4 mm., and the contents are mixed. To the mixture is added in five or six portions 15 c.c. of a solution of sodium molybdate containing 100 grams of molybdic anhydride per litre, the mixture being shaken after each addition. The tube is then spun in a centrifuge and when the separation of the three liquid phases is complete, the volume of the dense yellow liquid is read. The tube having been previously calibrated against a standard solution of a phosphate, the percentage of phosphoric anhydride in the solution under examination can at once be determined. If the solution contains citric acid or citrates, these must be removed by preliminary evaporation and ignition.

W. G.

Estimation of Phosphates in Waters. DANIEL FLORENTIN (*Ann. Chim. anal.*, 1921, 3, 295—296).—The colorimetric method described depends on the production of a blue colour when a dilute phosphoric acid solution is treated with ammonium molybdate in sulphuric acid solution and a small quantity of stannous chloride. Ten c.c. of the water to be tested are treated with two or three drops of molybdate reagent (100 c.c. of 10% ammonium molybdate

solution mixed with 300 c.c. of 50% sulphuric acid) and one drop of stannous chloride solution (0.1 gram of tin dissolved in 2 c.c. of hydrochloric acid and diluted to 10 c.c.). As little as 0.01 mg. of P_2O_5 per litre yields a distinct blue coloration, the intensity of which reaches a maximum in ten minutes. Comparison with the colorations given by known amounts of phosphoric acid gives the quantity of the latter present in the test solution. W. P. S.

Detection of Pyrophosphoric Acid in the Presence of Orthophosphoric Acid and Metaphosphoric Acid. D. BALAREFF (*Zeitsch. anal. Chem.*, 1921, 60, 385—392).—To detect pyrophosphoric acid in the presence of orthophosphoric acid, the solution containing the two acids is rendered slightly alkaline towards phenolphthalein, treated with a few drops of 5% copper sulphate solution and dilute acetic acid is added until the precipitate is just dissolved; a minute crystal of copper pyrophosphate is then introduced. A precipitate of copper pyrophosphate forms gradually. Another portion of the neutralised solution may be treated with silver nitrate and acetic acid; the latter dissolves the yellow silver orthophosphate, whilst the white pyrophosphate remains insoluble. If metaphosphoric acid is also present, the precipitate obtained with copper or silver salts must be further examined, since certain forms of metaphosphoric acid yield precipitates resembling those given by pyrophosphate. For this purpose, the precipitate is dissolved in nitric acid, the solution neutralised, then acidified with acetic acid, and tested with albumin solution for the presence of metaphosphoric acid. The reaction described by Berthelot and Andre (A., 1897, ii, 158, 283) is untrustworthy in the presence of metaphosphoric acid. W. P. S.

Detection of some Metals and of Arsenic in Plant and Human Organs. A. KEILHOIZ (*Pharm. Weekblad*, 1921, 58, 1482—1495).—The methods available for the detection of minute quantities of arsenic, copper, manganese, zinc, aluminium, and lithium have been examined, and a scheme has been drawn up and applied to the examination of the organs of the human body and of plants for these elements. The organic matter is destroyed by means of sulphuric and nitric acids, these are removed in the usual manner, and the residue is taken up in water.

Forty per cent. of the solution is examined for arsenic, 20% for lithium, and the remainder for copper, manganese, and zinc, which are removed in succession, the solution being finally examined for aluminium.

The Bloemendal modification of Marsh's apparatus was selected for the arsenic examination, the mirrors obtained being dissolved in excess of chromic acid, the excess being titrated with iodine. The arsenic in the mirror can also be determined by Ramberg's method, which depends on the reaction $As + 5I + 4H_2O = H_3AsO_4 + 5HI$; this is more suitable for exact determination of very small quantities, but requires a mechanical shaking apparatus. In the examination of urine it was found that organic arsenic compounds, such as cacodyl derivatives, are not destroyed by the ordinary

acid combustion; the permanganate method gives accurate results in these cases.

Copper is best determined electrolytically, using a platinum cathode in a platinum crucible, which serves as anode, a potential difference of 2 volts, and a current of 4—8 milliamperes. At 60—70°, two to four hours are required. The anode is weighed on a Köhlmann balance. Zinc and manganese do not interfere.

Manganese can be determined colorimetrically by Marshall's method (A., 1901, ii, 350) or electrolytically precipitated as peroxide. Zinc is best determined electrolytically in acetic acid solution in the cold. Aluminium is estimated colorimetrically with alizarin (Atack, A., 1915, ii, 842) and lithium spectroscopically.

Application of the methods worked out showed arsenic to be present sometimes in the liver, generally in urine, and in all the plants examined; copper and zinc generally in the liver, and in some plants; manganese in the liver, brains, and blood, and in some plants; aluminium was not found in human organs, but lithium was present in nearly every organ examined, and in all the plants. Tabulated results are given in milligrams of each element per kilogram of material examined. S. I. L.

New Type of Combustion Bomb made of Krupp's Special Steel. W. A. ROTH, R. MACHELEIDT, and IRMG. WIEMS (*Zeitsch. angew. Chem.*, 1921, 34, 537—538).—A new calorimeter combustion bomb designed to replace the usual type with platinised or enamelled interior is constructed of Krupp's special acid-resisting "V₂A" steel (20—23% Cr, 6—9% Ni, 0.1—0.3% C). The bomb, which is made of either the "Langbein" or "Kroeker" type, is provided with a quartz or porcelain dish in which the substance to be burnt is placed. This is suspended in the interior of the bomb, from two hooks in the electric leads. The insulated lead is a rod of the chrome nickel steel, and the other is a tube serving for the admission of oxygen and the egress of the gases from the combustion, and is made of silver, since a small bent tube cannot yet be constructed out of the steel alloy. The bomb can be used for the combustion of all ordinary organic substances, including nitro-compounds, but it is not available for substances containing halogens or a high percentage of sulphur, the alloy not being resistant to nascent sulphuric or halogen acids. Normally, with the former category of organic compounds, including coals with 5—7% of sulphur, only about 0.2 mg. of iron is dissolved, and no nickel. This would generate approximately 0.2 cal. With the latter class of substances several mg. of both iron and nickel are dissolved from the surface of the metal. The susceptibility to attack, however, appears to grow less with use, and substances with a comparatively high sulphur content can then be successfully burnt. G. F. M.

The Determination of the Degree of Oxidation of Coals. GEORGES CHARPY and GASTON DECORPS (*Compt. rend.*, 1921, 173, 807—811).—The oxidation of coal may take place in two ways. In the first, there is direct fixation of oxygen with a resulting increase in total weight and volatile matter. In the second, there

is simple oxidation with formation of carbon dioxide and water and a consequent diminution in total weight and a slight decrease in the percentage of volatile matter. The first reaction is the more important at low temperatures. The method proposed for determining the degree of oxidation of a sample of coal consists in powdering and sifting the coal and heating a known weight of it with 50% sodium hydroxide solution at 100° for two hours, using 10 c.c. of the solution for each gram of coal. The resulting liquid is diluted and filtered, the filtrate being acidified with sulphuric acid and made up to a known volume. To an aliquot portion an excess of standard potassium permanganate solution is added and the mixture is left at the ordinary temperature for two hours, after which the excess of permanganate is titrated back. In this way is determined the oxidation index, that is the number of grams of oxygen necessary to oxidise the organic matter dissolved by the sodium hydroxide from one kilo. of coal. Coals required to produce a resistant coke should, as a rule, have an oxidation index not exceeding 2. Curves are given showing the variation with time of the oxidation index and total weight of two samples of coal kept at 150°.

W. G.

Apparatus for the Estimation of Carbon Dioxide (in Carbonates). WILHELM KOHEN (*Chem. Zeit.*, 1921, 45, 1027).—The apparatus consists of a small reaction flask provided with a tapped funnel for the introduction of the acid; the neck of the flask is fitted with a small reflux condenser of the ball type, and this is connected with a sulphuric acid bulb and a potash bulb. The contents of the flask may be boiled to expel the last traces of carbon dioxide, the condenser and sulphuric acid bulb preventing any water vapour entering the potash bulb.

W. P. S.

A New Method of Estimating Silica. TRAVERS (*Compt. rend.*, 1921, 173, 714—717).—The silica is first converted into an alkali silicate and to it, in solution in a silver dish, is added at least 1 gram of potassium fluoride for every 0.15 gram of silica. Hydrochloric acid is added until the liquid is just neutral, and then a further 2 c.c. are added, and finally 7—10 grams of potassium chloride for every 50 c.c. of liquid. The precipitated potassium silicofluoride is collected on a hardened filter in an ebullition funnel and washed with a 20% solution of potassium chloride until free from acid. The wet precipitate is suspended in boiling water and titrated with $N/5$ potassium hydroxide, free from carbonate, using phenolphthalein as indicator. One c.c. of the alkali corresponds with 0.005 gram of silica. Details are given for the application of the method to the estimation of traces of silica in alkali hydroxides and salts, to the analysis of quartz and silicates, and to the estimation of silica in the presence of fluorine and aluminium.

W. G.

Gravimetric Estimation of Potassium by the Cobalt Method. A. VERTHEIM (*Rec. trav. chim.*, 1921, 40, 593—599).—A study of the conditions under which a precipitate of constant composition is given by potassium compounds with a cobalt salt

and sodium nitrite. Such a precipitate, apart from variations in water content, can be obtained: these variations are eliminated by drying at 110° to constant weight. The method is thus rendered of use for direct estimation.

H. J. E.

Estimation of Potassium in Soils and Fertilisers. HARALD R. CHRISTENSEN and NIELS FEHLBERG (*Landw. Versuchs.-Stat.*, 1921, 97, 27—56).—The cobaltinitrite method of Mitscherlich (A., 1912, ii, 204, 996) is modified, whereby 5 c.c. of saturated sodium chloride solution are added together with the precipitating reagent, thereby ensuring more complete precipitation. The method is applicable to the estimation of potassium in fertilisers and soil extracts. [See further *J. Soc. Chem. Ind.*, 1921, 820A.]

G. W. R.

The Acidimetric Estimation of Ammonium Salts with Formalin. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, 58, 1463—1469).—Formaldehyde reacts readily with ammonium salts in aqueous solution, forming hexamethylenetetramine and setting free the acid originally combined with the ammonia. The procedures of Gaillet (A., 1913, ii, 240) and of van Bers (A., 1917, ii, 578) have been found unsatisfactory. Very accurate results are obtained by adding 5 c.c. of formalin (B.P., neutral to phenolphthalein) to 25 c.c. of the solution (about 0.1 mol. per litre) of ammonium salt, and titrating the liberated acid after one minute with $N/10$ -sodium hydroxide solution. It is equally satisfactory to use excess of soda with the formalin, titrating the excess with acid after fifteen minutes.

The sodium hydroxide must be free from carbonate, and the water used for the solutions free from carbon dioxide; phenolphthalein is used as indicator. Small quantities of neutral salts do not interfere. The method is not suitable for the accurate estimation of formaldehyde.

S. I. L.

Chemical Analysis with Membrane Filters. II. Volumetric Estimation of Zinc. GERHART JANDER and HANS CAESAR STUHLMANN (*Zeitsch. anal. Chem.*, 1921, 60, 289—321; cf. A., 1919, ii, 520).—The collection and washing of zinc sulphide precipitates are facilitated by the use of membrane filters; the sulphide should be precipitated from an acetic acid solution containing sodium acetate. Of volumetric methods for the estimation of zinc sulphide, Mann's method (decomposition of the zinc sulphide with moist silver chloride and subsequent titration of the zinc chloride) and acidimetric methods are trustworthy.

W. P. S.

Sensitive Reaction for Copper. P. FALCIOLA (*Giorn. Chim. Ind. Applic.*, 1921, 3, 354—355).—Cupric salts may be detected in solution even in 0.00001 N -concentration, by means of alkali thiocyanate solution mixed with cold saturated gallic acid solution, a decided turbidity being produced. The cupric solution should be neutral and free from silver, lead, and bismuth. Similar precipitation of copper occurs if the gallic acid in the reagent is replaced by tannic acid, catechol, or quinol, but not by resorcinol. [Cf. *J. Soc. Chem. Ind.*, 1921, Dec.]

T. H. P.

Rapid Electro-analysis of Brass. A. LASSIEUR and (MME) A. LASSIEUR (*Compt. rend.*, 1921, 173, 772—775).—The following details of working should be strictly adhered to. 0.5 Gram of brass in the form of thin foil is dissolved in 20 c.c. of sulphuric acid (50% by weight) and 1 c.c. of nitric acid (*d* 1.33), the liquid being heated to boiling at first. When solution is complete, the liquid is diluted to 70 c.c. with water and electrolysed, using a current of 4–5 amperes and rotating electrodes. The operation lasts forty minutes, during which the whole of the copper is deposited and the nitric acid is completely reduced. To the liquid, freed from copper and containing the rinsings of the electrodes, are added 25 c.c. of sodium hydroxide (*d* 1.33), 15 c.c. of glacial acetic acid, and 10 c.c. of a saturated solution of sodium fluoride in the order named. The liquid is cooled to the ordinary temperature and electrolysed, the zinc being deposited on a copper-coated cathode, using a current of 4 amperes. In some cases, at the end of the first electrolysis a slight deposition of zinc is noted. This zinc at once dissolves again when the current is stopped. W. G.

The Separation of Aluminium from Glucinum. II. HUBERT T. S. BRITTON (*Analyst*, 1921, 46, 437—445; cf. this vol., ii, 657).—Aluminium cannot be separated from glucinum satisfactorily by means of ammonium carbonate in either hot or cold solutions, as not only does the precipitated aluminium hydroxide carry down considerable amounts of glucina, but much alumina remains in the ammonium carbonate solution. Treatment of a solution of the two metals with ammonium sulphite yielded, on boiling, a precipitate containing all the aluminium and much glucinum, although the latter alone gives no precipitate with the reagent. Separation by means of sodium hydrogen carbonate (Parsons and Barnes, A., 1907, ii, 52) yields satisfactory results if neither the glucinum nor aluminium in 100 c.c. of the solution saturated with sodium hydrogen carbonate exceeds 0.15 gram, and if the adsorption in both precipitations is kept at a minimum by vigorous stirring. A. R. P.

Reaction of Manganese, Iron, and Cobalt. D. BALAREFF (*Zeitsch. anal. Chem.*, 1921, 60, 392—393).—The precipitate containing manganese and iron hydroxides is washed, dissolved in nitric acid, the solution boiled to oxidise ferrous salt, then neutralised with sodium hydroxide solution, treated with silver nitrate solution, and then rendered ammoniacal or acidified with acetic acid; in the presence of as little as 0.2 mg. of manganese per litre, a black precipitate is observed in the ammoniacal solution, or a yellowish-brown precipitate in the acetic acid solution. Cobalt and ferrous salts yield a similar reaction. W. P. S.

Titration with Potassium Permanganate. ANT. JLEK (*Chem. Listy*, 1921, 15, 105—109, 138—140).—The titration of sodium oxalate, oxalic acid, ferrous ammonium sulphate, and electrolytic iron (prepared according either to Treadwell or Classen) was studied. The results of these titrations agreed with each other more closely if the volumes of 0.1N-potassium permanganate used

were approximately equal. Treadwell's method did not require a control estimation. Standardisation against sodium oxalate, oxalic acid, and ferrous ammonium sulphate is very facile and accurate. Classen's method was rapid and accurate, if the iron dissolved in sulphuric acid is titrated in the presence of platinum. Solutions of 0.1*N*-ferrous sulphate, slightly acidified with sulphuric acid, and exposed to air, are practically unaffected after twenty-four to forty-eight hours. There is practically no danger of the oxidation of these solutions during their filtration through paper or glass wool.

CHEMICAL ABSTRACTS.

Volumetric Estimation of Mixtures of Permanganate, Dichromate, and Chromic Salts. NITYA GOPAL CHATTERJI (*Chem. News*, 1921, **123**, 232—233).—The method depends on the fact that permanganate is converted into hydrated manganese dioxide by treatment with a solution containing manganese sulphate and zinc sulphate, whilst dichromate is not affected. Titration of a mixture of permanganate and dichromate with ferrous sulphate solution before and after such treatment gives a measure of the amounts of the two substances present. The estimation of chromium salts is based on their oxidation to dichromate by heating with hydrated manganese dioxide in dilute sulphuric acid solution.

W. P. S.

The Iodometric Determination of Iron. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 1510—1522).—The slowness of the reaction between ferric salts and iodides is found to be due to the hydrolysis of the former, resulting in the formation of colloidal ferric hydroxide. Strong acids accelerate the reaction, but not if present in excess, since complex ferric salts are formed. The reaction is very suitable for analytical work if the iron solution be about *M*/10, and the correction concentration of acid and iodide be obtained. For 25 c.c. of iron solution, about 2 c.c. of concentrated hydrochloric acid (25—39%) and 1.6 grams of potassium iodide are required; after fifteen minutes, the iodine is titrated with thiosulphate. Sulphates and oxalates interfere; phosphates interfere only if the solution is not sufficiently acidic. Even ferric solutions as dilute as 0.001 *M* can be accurately titrated in *N*/10-hydrochloric acid solution if sufficient iodide (0.5 gram for 10 c.c. of iron solution) be used.

S. I. L.

The Different Methods of Attack of Ochreous Minerals. A. RAYNAUD (*Bull. Soc. chim.*, 1921, [iv], **29**, 905—910).—For the analysis of the ochres, 0.5 gram of the finely-powdered mineral, previously dried at 100—105°, is weighed into a platinum crucible, strongly ignited for a few minutes, and weighed again. The loss in weight is due to water of combination and traces of carbonate and organic matter. To the residue 4—5 c.c. of dilute sulphuric acid and 8—10 c.c. of fuming hydrofluoric acid are added, and the mixture is evaporated to dryness at a gentle heat, finally heated more strongly until fuming has ceased, and then ignited. The residue, which consists of oxides of iron and alumina, is weighed,

the loss in weight by the acid treatment being reckoned as silica. The residue is fused with potassium hydrogen sulphate, and after rapid cooling the fused mass is extracted with water, the iron reduced to the ferrous state, and estimated by titration with permanganate. The percentage of aluminium oxide is got by difference from the mixed oxides. The process is rapid and gives results quite comparable with those obtained with more complicated methods.

W. G.

Application of Amalgams in Volumetric Analyses. II. Estimation of Vanadium and Uranium. TAMAKI NAKAZONO (*J. Chem. Soc. Japan*, 1921, 42, 761—768; cf. this vol., ii, 596).—Vanadium can be titrated with potassium permanganate either by reduction to (a) the bivalent state by shaking with liquid zinc amalgam for three minutes in the absence of air in the manner previously described (*loc. cit.*), or (b) to the quadrivalent state by treatment with saturated silver sulphate solution, after shaking with zinc amalgam for three seconds only.

Uranium is titrated with potassium permanganate after reduction to the quadrivalent state by shaking with zinc amalgam for thirty seconds in the presence of air.

K. K.

Estimation of Fermentation Glycerol. KARL FLEISCHER (*Zeitsch. anal. Chem.*, 1921, 60, 330—338).—One hundred c.c. of the glycerol solution (obtained by the fermentation process) is distilled under reduced pressure with superheated steam, the temperature of the distillation flask being raised gradually to 250°; the distillate is collected in a flask immersed in a water-bath at 70°. This receiving flask is provided with a reflux apparatus supplied with a current of water at 70°, and the top of the reflux apparatus is connected with an ordinary condenser, receiver, and pump. When glycerol ceases to collect in the flask, the steam supply is cut off, and the contents of the flask are heated at 100° under reduced pressure until practically all water has been removed; a small current of air is admitted to the flask through a capillary to aid in the removal of the water. The residue of glycerol in the flask is then weighed; its specific gravity is determined so that an allowance can be made for the small quantity of water still present.

W. P. S.

Sugar Calculations. J. F. LIVERSEEGE (*Analyst*, 1921, 46, 446—450).—Equations are given for correcting the specific rotatory power of a sugar or mixture of sugars for temperature and concentration and examples are given of the method of calculating the proportions of the various commercial sugars in solutions from the observed specific rotatory power before and after inversion, the value of *K* (that is, reduction expressed as dextrose and laevulose) before and after fermentation, and the total organic solids. A table of constants and factors for the more important sugars is also given.

A. R. P. *

Estimation of the Pentose Sugars. HERMAN AUGUSTUS SPOEHR (*Carnegie Inst. Pub.*, 1919, No. 287, 36—37).—The hexose sugars

are fermented with baker's yeast, and the alcohol and other products of fermentation are removed by distillation. The residual solution containing pentoses is then caused to react with hot Fehling solution, and the cuprous oxide obtained by reduction is estimated by an iodometric titration. The non-fermentable sugar must be recognised as pentose by the proper tests.

CHEMICAL ABSTRACTS.

The Quantitative Estimation of Dextrose and Lævulose in a Solution. HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1921, 118, 120—128).—The optical rotation of the solution, and the total reducing power on copper sulphate by Pflüger's method (*Pflüger's Archiv*, 1906, 114, 242) for dextrose are determined. Pflüger's table of reducing powers of dextrose in terms of cuprous oxide is used as the standard of reference for dextrose, and an analogous table is experimentally determined for lævulose. Knowing the optical rotation of dextrose and lævulose separately, the content of dextrose and of lævulose is determined graphically or by simple calculation.

H. K.

Comparative Estimations of Lignin in Cellulose. E. HEUSER and G. WENZEL (*Papierfabr.*, 1921, 19, 1177—1184).—The degree of accuracy of a number of methods for the estimation of lignin has been compared using a sample of unbleached, rasped Mitscherlich sulphite-cellulose, which gave the qualitative reactions for lignin distinctly, with a total solid content of 91.5%, benzene-alcohol extract (resin and fat) 1.48%, and ash 0.85%. The estimation of lignin by Becker's modification (*Papierfabr.*, 1919, 17, 1325) of König and Rump's method (*Zeitsch. Unters. Nahr. Genussm.*, 1914, 28, 184) using 72% sulphuric acid, gives too high results, owing to the separation on dilution of colloidal products which contain no lignin, but are weighed as such. Too high results are also obtained by König and Becker's modification (*Papierfabr.*, 1919, 17, 565) of Krull's method (*Diss., Danzig*, 1916, 19) using gaseous hydrogen chloride, and König and Rump's method (*loc. cit.*) using dilute hydrochloric acid under pressure, owing to the incomplete saccharification of the cellulose. On the other hand, trustworthy determinations of lignin in cellulose are obtained by a modification of Willstätter and Zechmeister's method (*A.*, 1913, i, 955), in which 1 gram of the sample is covered with 70 c.c. of 41.4% hydrochloric acid in a stoppered flask, frequently shaken during eighteen hours, diluted with ten times the volume of water, and boiled for ten minutes.

F. M. R.

Estimation of Lactic Acid in Blood. G. A. HARROP, jun. (*Proc. Soc. Expt. Biol. Med.*, 1920, 17, 126—133).—The method is based on Denigès's observation that lactic acid is converted by concentrated sulphuric acid into acetaldehyde, and can be estimated with phenols and morphine alkaloids. Five c.c. of blood or serum are heated for 4—5 minutes on a water-bath with 15 c.c. of acidified copper sulphate solution, and excess of powdered calcium hydroxide is added to the cold liquid. After thirty minutes, it is filtered, and one part of the filtrate is added to four parts of concentrated sulphuric acid while the mixture is being shaken and cooled in water.

at 0°. After being placed in a boiling-water bath for two minutes, it is again cooled to 0°, three drops of a 5% solution of guaiacol are added, and after keeping for twenty minutes the rose colour which has developed is compared with standards similarly prepared.

CHEMICAL ABSTRACTS.

A Modification of Aschman's Method of Determining the Iodine Value. B. M. MARGOSCHES and R. BARU (*Chem. Umschau*, 1921, 28, 229—232 and 245—247).—The iodine monochloride solution is prepared as follows: 15 grams of potassium iodide are dissolved in 50 c.c. of water and chlorine is passed through until the iodine at first precipitated is completely redissolved. The solution is left for five hours, and is then decanted from the crystalline precipitate, which is washed, and the solution and washings are made up to 500 c.c. with water. The solution is even more stable than Wijs's solution.

0.5—0.1 Gram of the oil or fat (according to the iodine value expected) is taken and dissolved in 10 c.c. of carbon tetrachloride and 10 c.c. of the iodine monochloride solution are added. The mixture is shaken and it is essential that the shaking is repeated two or three times during the first half of the absorption period, which varies from two to four hours for fats, six hours for non-drying, eight hours for semi-drying, and twenty-four hours for drying oils when only 60% excess of iodine is used. The time can be reduced by using a larger excess (75%) when six to eight hours are sufficient even for drying oils. The excess of iodine is titrated in the usual way. An iodine monochloride solution of half the above concentration can be used equally well. The values obtained usually lie between the corresponding Hübl and Wijs values. H. C. R.

A Modified Babcock Method for Determining Fat in Butter. N. W. HEPBURN (*Cornell Univ. Agric. Exp. Sta., Memoir* 37, 669—690).—The size of the bottle used in the Babcock cream test is modified to suit the fat estimation in butter. A 23 cm. bottle is used for 9 gram samples and a 15 cm. for 6 gram samples, the diameter of the graduated part of the neck being 9.07 and 9.04 mm. respectively for the two sizes. With the former, the semi-solid butter is covered with 9 c.c. of lukewarm water, and 17.6 c.c. of commercial sulphuric acid are added slowly and with vigorous shaking, followed by more water to bring the liquid to the graduation marks. After five minutes' centrifuging, more water is added to bring the liquid again to the graduations. The bottle is again centrifuged for four minutes and placed in a water-bath at 52—54°, and the volume of fat is read off. Glymol may be used to flatten the meniscus. The results obtained compare favourably with those from chemical analyses. The accuracy is the same with both sizes of bottle, but the 23 cm. is more easily manipulated. A. G. P.

The Estimation of Enols by Hieber's Copper Acetate Method. W. DIECKMANN (*Ber.*, 1921, 54, [B], 2251—2254; cf. Hieber, this vol., ii, 466).—Hieber's method for the estimation of enols is not valid, since it depends on the assumption that the com-

plex copper salts of the latter are not affected under the experimental conditions (in alcohol-chloroform solution in the presence of an equimolecular amount of copper acetate) by an equivalent amount of acetic acid. This is true only of the copper salts of strongly acidic enols, for example, α -mesityloxideoxalic ester, but not of those derived from ethyl acetoacetate and similar substances of a more feebly acidic nature. Repetition of Hieber's experiment with "equilibrium ethyl acetoacetate" or with a specimen containing a larger proportion of enol leads to the formation of about 7.5% of the copper salt which is produced to the extent of about 11% when the quantity of copper acetate is doubled, and about 14% when the quantity is quadrupled. The reaction between ethyl acetoacetate and copper acetate does not depend on the combination of the enolic form, but on the attainment of an equilibrium between the copper compound of ethyl acetoacetate, copper acetate, and acetic acid, which, in consequence of the rapid keto-enolic transformation, is independent of the enol content of the ethyl acetoacetate. The coincidence of Hieber's datum with the known enolic content of "equilibrium ethyl acetoacetate" is purely accidental and depends on the experimental conditions and relative quantities of material; the remarkable agreement shown in other instances is doubtless conditioned by the fact that, in accordance with Classen's rule, acidity and tendency towards enolisation are, in general, parallel characteristics. The copper salts of other enols show an analogous but gradually differing behaviour from that of the compound derived from ethyl acetoacetate. The figures enclosed within the brackets represent the percentages of the substances which remain unchanged after treatment with two molecular proportions of acetic acid and one of copper acetate in alcohol-chloroform solution: ethyl copper benzoylacetate (ca. 38), copper acetylacetone (60), ethyl copper oxalacetate (ca. 85), copper benzoylacetone (ca. 100), methyl copper α -mesityloxide oxalate (ca. 100).

Hieber's method is applicable only in the few cases in which the copper salt is not attacked by acetic acid and the rate of keto-enolic transformation is so small that an alteration of the enolic content does not occur during the course of the experiment. H. W.

Estimation of Citronellol and Citronellal by Formylation.

C. T. BENNETT (*Perf. and Essent. Oil Rec.*, 1921, 12, 351).—The formic acid method for the estimation of citronellol and citronellal is absolutely untrustworthy. Even with pure citronellol, the results were high when 100% acid was used, and low with a weaker acid, and in the case of mixtures, such as otto of rose, the results are vitiated by the action of the acid on the geraniol present, which it partly converts into formate. The action of 100% formic acid on citronellol yields a mixture of products containing unchanged citronellol, a small amount of what is probably an aliphatic or cyclic terpene, citronellol formate, b. p. 99–100°/7 mm., the compound $\text{OH}\cdot\text{CMe}_2\cdot(\text{CH}_2)_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CHO}$, b. p. 129°/5 mm. $d=0.9651$, $\mu=1.4488$, $\alpha=1^\circ 46''$, and the corresponding diformate, b. p. 140–141°/7 mm. G. F. M.

The Acid Amide Fraction of the Nitrogen of Peat. E. J. MILLER and C. S. ROBINSON (*Soil Sci.*, 1921, **11**, 457—467).—It is shown that both glutamic acid and aspartic acid are obtainable from peat by hydrolysis with hydrochloric acid. Attempts to separate glutamic acid directly from the hydrolysate were not successful. The application of Foreman's method (cf. A., 1914, ii, 826) in a slightly modified form resulted in the separation of both glutamic and aspartic acids, and in the estimation of pyrrolidonecarb. oxylic acid from the hydrolysate. W. G.

Estimation of Cyanides Iodometrically with the aid of Benzene. NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1921, **42**, 454—462).—Benzene can be used as an indicator in iodometry for the accurate estimation of cyanides. The original solution is mixed with 1% boric acid solution, then with the same quantity of 1% borax solution, and titrated; or impurities in the original solution are removed by addition of sodium hydrogen carbonate and after neutralisation with hydrochloric acid, the titration is performed. In each case, benzene is added to indicate the end point; when the benzene is tinged, sodium hydrogen carbonate is added, and the titration continued. The method is applicable in general iodometry, when the sample is coloured strongly or contains precipitates. The method has been used in analysing samples of potassium chromate and potassium ferrieyanide. K. K.

Estimation of Thiocyanate in the Presence of Salts which Precipitate Silver Nitrate. ANDRÉ DUBOSC (*Ann. Chim. anal.*, 1921, **3**, 297—298).—To estimate thiocyanate in the presence of chlorides, etc., the sulphur in the thiocyanate is oxidised to sulphate and then precipitated as barium sulphate. The oxidation is best made with a reagent prepared by electrolysis of a mixture of sodium chloride and magnesium chloride solutions; this reagent should contain 2% of "active" chlorine. A suitable quantity of the thiocyanate is dissolved in 50 c.c. of water, 50 c.c. of 4% barium chloride solution and 50 c.c. of the reagent are added, and after ten minutes, the mixture is acidified with 10 c.c. of hydrochloric acid, boiled, and the barium sulphate collected and weighed. W. P. S.

The Estimation of Creatinine in the Presence of Acetone and Acetoacetic Acid. NATHAN F. BLAU (*J. Biol. Chem.*, 1921, **48**, 105—118).—The author demonstrates, by numerous analyses, the disturbing effects of the presence of acetone substances on the estimation of creatinine by the method of Folin. He describes a method of removing these interfering substances from urine by boiling, the temperature being kept low by the addition of methyl alcohol. C. R. H.

Estimation of the Alkaloid Content of Lupines. F. MACH and P. LEDERLE (*Landw. Versuchs.-Stat.*, 1921, **98**, 117—124).—The authors discuss the errors which may occur in the estimation of the alkaloid content of lupines by extraction with chloroform-ether and precipitation of the alkaloids by silicotungstic acid. Calculation of the alkaloid content from the weight of residue

